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THE NEUTRINO THEORY OF LIGHT—II.

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1. Introduction.

When we published our report[1] on Jordan's[2] neutrino theory of light in these *Proceedings*, we assumed a standpoint differing in some respects from Jordan's[3] and Kronig's[4] initial papers. Meanwhile they have published new representations[5] of the theory which are in complete agreement with our report. The point is that the theory as presented on the basis of the Dirac theory of holes in our report which is followed recently in Jordan's[6] last paper, deals with two kinds of neutrinos—neutrinos and anti-neutrinos—but neglects the spin.

But there is no doubt that neutrinos have a spin. There is the general theorem that particles with an integral angular momentum must obey the Bose–Einstein statistics and that particles with a half-integral angular momentum must obey the Fermi-Dirac statistics.[7] Empirical evidence for the existence of the spin is afforded by the theory of β-decay*; if electron, proton and neutron have each of them the spin $\frac{1}{2}$, then the process

$$\text{neutron} \rightarrow \text{proton} + \text{electron} + \text{neutrino}$$

[1] M. Born and N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1936, **3**, 318. (Referred to as I)
[2] P. Jordan, *Zeits. f. Phy.*, 1935, **93**, 464.
[3] P. Jordan, *Zeits. f. Phy.*, 1936, **98**, 709 and 759; 1936, **99**, 109.
[4] R. de L. Kronig, *Physica*, 1935, **2**, 491, 854, 965.
[5] P. Jordan and R. de L. Kronig, *Zeits. f. Phy.*, 1936, **100**, 569.
[6] P. Jordan, *Zeits. f. Phy.*, 1936, **102**, 243.
[7] P. Jordan, *Anschauliche Quantenmechanik* (Julius Springer), 1936, p. 244.

* This argument implies the identity between Jordan's neutrino which is the fundamental particle in his theory of light, and Pauli's neutrino whose existence has been assumed to account for β-decay. Experimental evidence on β-decay seems to show that Pauli's neutrino has practically no charge and no rest mass. Thus, the common characteristics between Jordan's neutrino and Pauli's neutrino in that they have no rest mass and no electrical charge, constitute strong arguments to believe that Jordan's neutrino and Pauli's neutrino are identical. An experimental proof for this identification might result by studying a possible influence of light field on β-decay.

shows that the neutrino must also have the spin $\frac{1}{2}$. Another argument is that the spin of the neutrino is necessary to account for the polarisation of light. Indeed the theory which neglects the spin (as in I and in Jordan's papers) leads to half the value given by Planck's formula which can easily be understood by the consideration that the internal degree of freedom of the neutrinos (spin) and of the photons (polarisation) is not incorporated in the formalism.

One of us[8] has shown how the spin can be easily introduced by adding a corresponding index to the operators representing neutrinos $a_{\kappa,i}$ where $i = \mathrm{R}, \mathrm{I}$, characterising the two spin states. A photon state is then represented by a *pair* of operators ; namely,

$$b_{k,\rho} = \frac{-1}{\sqrt{|2k|}} \sum_{\kappa=-\infty}^{\infty} \sum_{i} a_{\kappa,i}\, a_{\kappa}{}^{\dagger}{}_{-k,i}$$

$$b_{k,\lambda} = \frac{-1}{\sqrt{|2k|}} \sum_{\kappa=-\infty}^{\infty} \sum_{i,j}{}' a_{\kappa,i}\, a_{\kappa}{}^{\dagger}{}_{-k,j}$$

where the dash over the (i, j) summation indicates that $i \neq j$ and ρ and λ characterise the two polarisation states of light. Though this method leads to correct results, for instance Planck's formula, it is not very satisfactory from the formal standpoint. We shall present here a new form of this theory in which each physical quantity belongs to only *one* operator. The fundamental matrices representing them have now of course four rows and columns instead of those of two in the earlier representations. This procedure is in better agreement with the general definitions of quantum mechanics and leads to very simple and elegant results.

2. *The Operators of the Neutrino Field.*

The neutrino field is described by two sets of infinite numbers of non-commuting operators a_κ and γ_κ which are enumerated by half-integral positive numbers, $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\ldots$ The half-integral numbers are chosen primarily for the sake of convenience. The operators with negative indices are defined by the relations

$$\kappa > 0, \quad a_{-\kappa} = \gamma_{\kappa}{}^{\dagger}, \quad \gamma_{-\kappa} = a_{\kappa}{}^{\dagger}\,; \tag{2.1}$$

where † means the adjoint operator. Indeed, one may see by (2.1) that there is no necessity for the introduction of two sets of operators but we retain them, following Jordan, for the sake of symmetry between neutrinos and anti-neutrinos whose relations with the above operators will be defined subsequently. The meaning of these operators can be understood with the help of the Correspondence Principle as the Fourier coefficients of the wave

[8] N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1936, **3**, 448.

functions which will be in the case of one dimension

$$\begin{aligned}\psi\,(t - x/c) &= \sum_{\kappa=-\infty}^{\infty} a_\kappa \exp\,[2\pi i\nu_1\kappa\,(t - x/c)],\\ \chi\,(t - x/c) &= \sum_{\kappa=-\infty}^{\infty} \gamma_\kappa \exp\,[2\pi i\nu_1\kappa\,(t - x/c)] = \psi^\dagger,\end{aligned} \tag{2.2}$$

where ν_1 corresponds to the fundamental frequency of the " Hohlraum ".

We postulate the following commutation rules for the operators :

$$\begin{aligned}a_\kappa\, a_\mu + a_\mu\, a_\kappa &= 0,\\ \gamma_\kappa\,\gamma_\mu + \gamma_\mu\,\gamma_\kappa &= 0,\\ \gamma_\kappa\, a_\mu + a_\mu\,\gamma_\kappa &= \delta_{\mu,-\kappa},\end{aligned} \tag{2.3}$$

where $\delta_{\mu,-\kappa}$ is the Dirac operator which is zero if $\mu \neq -\kappa$ and is the unit matrix if $\mu = -\kappa$. The operators describing the number of neutrinos and anti-neutrinos of energy κ (the unit of energy being $h\nu_1$) are defined only for $\kappa > 0$ by

$$\begin{aligned}\mathrm{N}_\kappa^{(+)} &= a_\kappa^\dagger\, a_\kappa = 1 - a_\kappa\, a_\kappa^\dagger,\\ \mathrm{N}_\kappa^{(-)} &= \gamma_\kappa^\dagger\,\gamma_\kappa = 1 - \gamma_\kappa\,\gamma_\kappa^\dagger.\end{aligned} \tag{2.4}$$

The relations

$$\begin{aligned}a_\kappa^\dagger\, a_\kappa &= 1 - a_\kappa\, a_\kappa^\dagger,\\ \gamma_\kappa^\dagger\,\gamma_\kappa &= 1 - \gamma_\kappa\,\gamma_\kappa^\dagger,\end{aligned} \tag{2.5}$$

are true in virtue of (2.3) and (2.1).

3. *The Fundamental Operators and Their Properties.*

In I, we started with the matrices

$$a = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix},\quad a^\dagger = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix} \text{ and } s = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}, \tag{3.1}$$

which have the following properties :

$$\begin{aligned}&a^2 = 0, \qquad a^{\dagger 2} = 0, \qquad s^2 = 1,\\ &a^\dagger a + a\,a^\dagger = 1, \quad as + sa = 0, \quad a^\dagger s + sa^\dagger = 0.\end{aligned} \tag{3.2}$$

We may note that the above matrices are related to Pauli's spin matrices by the equations

$$\sigma_x = a^\dagger + a,\ \sigma_y = i\,(a^\dagger - a) \text{ and } \sigma_z = s. \tag{3.3}$$

We build the fundamental matrices of the present theory by the above matrices of the old one and with the notion of the direct product of the matrices defined in I. The fundamental matrices are here defined as

$$\begin{aligned}\mathrm{A} &= a \times \mathbf{1}\\ \mathrm{S} &= s \times \mathbf{1}\end{aligned} \tag{3.4}$$

Corresponding to the rule of the direct product of matrices $\mathrm{A}_{n_1n_2;\,m_1m_2} = a_{n_1m_1}\,\mathbf{1}_{n_2m_2}$ and re-enumerating the combinations of the suffixes 11, 12, 21, 22,

as 1, 2, 3, 4 we find

$$A = a \times \mathbf{1} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad A^\dagger = a^\dagger \times \mathbf{1} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix},$$

$$S = s \times \mathbf{1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \tag{3.5}$$

We then have

$$AS = as \times \mathbf{1} = -a \times \mathbf{1} = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$SA = sa \times \mathbf{1} = a \times \mathbf{1} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{3.6}$$

from which we conclude

$$AS + SA = 0. \tag{3.7}$$

It is easy to see that

$$\begin{aligned} A^\dagger S + SA^\dagger &= 0, \\ A^2 = AA &= 0, \\ A^{\dagger 2} = A^\dagger A^\dagger &= 0, \\ S^2 = SS &= \mathbf{1}. \end{aligned} \tag{3.8}$$

The products $A^\dagger A$ and $AA^\dagger$ are given by

$$A^\dagger A = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$AA^\dagger = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{3.9}$$

which show that the matrix $A^\dagger A$ has the eigen-values 0, 0, 1 and 1 while $AA^\dagger$ has the same eigen-values in the reverse order. It is also to be seen that

$$A^\dagger A + AA^\dagger = \mathbf{1}. \tag{3.10}$$

The relations between the fundamental operators and Dirac's matrices.—We note that our matrices A and S can be expressed in terms of Dirac's[9] matrices.

[9] P. A. M. Dirac, *Quantum Mechanics*, page 255.

The Dirac matrices are

$$\rho_1 = \begin{pmatrix} 0&0&1&0 \\ 0&0&0&1 \\ 1&0&0&0 \\ 0&1&0&0 \end{pmatrix}, \quad \rho_2 = \begin{pmatrix} 0&0&-i&0 \\ 0&0&0&-i \\ i&0&0&0 \\ 0&i&0&0 \end{pmatrix}, \quad \rho_3 = \begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&-1&0 \\ 0&0&0&-1 \end{pmatrix} \tag{3.11}$$

$$\sigma_x = \begin{pmatrix} 0&1&0&0 \\ 1&0&0&0 \\ 0&0&0&1 \\ 0&0&1&0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0&-i&0&0 \\ i&0&0&0 \\ 0&0&0&-i \\ 0&0&i&0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1&0&0&0 \\ 0&-1&0&0 \\ 0&0&1&0 \\ 0&0&0&-1 \end{pmatrix},$$

$$\alpha_x = \rho_1 \sigma_x, \qquad \alpha_y = \rho_1 \sigma_y, \qquad \alpha_z = \rho_1 \sigma_z.$$

It is now easy to see that

$$\begin{aligned} \mathrm{A} &= \tfrac{1}{2}(\rho_1 + i\rho_2), \\ \mathrm{A}^\dagger &= \tfrac{1}{2}(\rho_1 - i\rho_2), \\ \mathrm{S} &= \rho_3 \end{aligned} \tag{3.12}$$

or

$$\begin{aligned} \rho_1 &= \mathrm{A}^\dagger + \mathrm{A} \\ \rho_2 &= i(\mathrm{A}^\dagger - \mathrm{A}) \\ \rho_3 &= \mathrm{S} \end{aligned} \tag{3.13}$$

closely resembling the relations (3.3) which exist between Pauli's matrices and the two-dimensional matrices of the old theory. We also note that we may choose for the development of the present theory $\frac{1}{2}(\alpha_x + i\alpha_y)$, $\frac{1}{2}(\alpha_x - i\alpha_y)$ and σ_z as the fundamental operators which may be expressed in terms of a, $a^\dagger$ and s.

Replacing the enumeration, 1, 2, 3, 4 by 0, $\bar{0}$, 1 and $\bar{1}$ the matrix elements of the fundamental matrices which do not vanish are given by

$$\begin{aligned} &\mathrm{A}(0,1) = 1, \qquad \mathrm{S}(0,0) = 1, \\ &\mathrm{A}(\bar{0},\bar{1}) = 1, \qquad \mathrm{S}(\bar{0},\bar{0}) = 1, \\ &\mathrm{A}^\dagger(1,0) = 1, \qquad \mathrm{S}(1,1) = -1, \\ &\mathrm{A}^\dagger(\bar{1},\bar{0}) = 1, \qquad \mathrm{S}(\bar{1},\bar{1}) = -1. \end{aligned} \tag{3.14}$$

4. The Jordan-Wigner Representations of the Operators.

As in I, we can write down the Jordan-Wigner representations of the neutrino operators by the following scheme:

$$\begin{array}{lccccccccccccc} & \frac{1}{2} & -\frac{1}{2} & & & -(\kappa-1) & & \kappa & -\kappa & (\kappa+1) & & & \\ a_\kappa = \gamma_{-\kappa}^\dagger = & \mathrm{S} & \times & \mathrm{S} & \times & \cdots & \times & \mathrm{S} & \times & \mathrm{A} & \times & \mathbf{1} & \times & \cdots \\ a_{-\kappa} = \gamma_\kappa^\dagger = & \mathrm{S} & \times & \mathrm{S} & \times & \cdots & \times & \mathrm{S} & \times & \mathrm{S} & \times & \mathrm{A}^\dagger & \times & \mathbf{1} & \times & \cdots \end{array}$$

$\kappa > 0$ (4.1)

$$\begin{array}{lccccccccccccc} \gamma_\kappa = a_{-\kappa}^\dagger = & \mathrm{S} & \times & \mathrm{S} & \times & \cdots & \times & \mathrm{S} & \times & \mathrm{S} & \times & \mathrm{A} & \times & \mathbf{1} & \times & \cdots \\ \gamma_{-\kappa} = a_\kappa^\dagger = & \mathrm{S} & \times & \mathrm{S} & \times & \cdots & \times & \mathrm{S} & \times & \mathrm{A}^\dagger & \times & \mathbf{1} & \times & \mathbf{1} & \times & \cdots \end{array}$$

Each matrix has only two types of non-vanishing elements which are given by the following scheme in which t_κ is 0, $\bar{0}$, 1, $\bar{1}$. They are

$$a_\kappa\left(t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, \overset{0}{\underset{}{0}}, t_{-\kappa}, - -; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, \overset{1}{\underset{}{1}}, t_{-\kappa}, - -\right) = (-1)^{p_{\frac{1}{2}}+p_{-\frac{1}{2}}+\cdots+p_{-(\kappa-1)}}$$

$$a_{-\kappa}\left(t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, t_\kappa, \overset{1}{\underset{}{1}}, - -; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, t_\kappa, \overset{0}{\underset{}{0}}, - -\right) = (-1)^{p_{\frac{1}{2}}+p_{-\frac{1}{2}}+\cdots+p_\kappa}$$

$\kappa > 0$ (4.2)

$$\gamma_\kappa\left(t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, t_\kappa, \overset{0}{\underset{}{0}}, - -; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, t_\kappa, \overset{1}{\underset{}{1}}, - -\right) = (-1)^{p_{\frac{1}{2}}+p_{-\frac{1}{2}}+\cdots+p_\kappa}$$

$$\gamma_{-\kappa}\left(t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, \overset{1}{\underset{}{1}}, t_{-\kappa}, - -; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, - -, \overset{0}{\underset{}{0}}, t_{-\kappa}, - -\right) = (-1)^{p_{\frac{1}{2}}+p_{-\frac{1}{2}}+\cdots+p_{-(\kappa-1)}}$$

where

$$p_\kappa = 0 \quad \text{if } t_\kappa = 0 \text{ or } \bar{0},$$
$$p_\kappa = 1 \quad \text{if } t_\kappa = 1 \text{ or } \bar{1}.$$

Using the definition of the direct product of the matrices and the equations (3.7), (3.8) and (3.10), it can easily be verified that the representations of the fundamental operators given in (4.1) satisfy the commutation rules (2.3).

5. *A New System of Operators.*

As in I, we introduce a new system of operators defined by

$$a_\kappa = \frac{a_\kappa + \gamma_\kappa}{\sqrt{2}}, \qquad c_\kappa = \frac{a_\kappa - \gamma_\kappa}{i\sqrt{2}}, \tag{5.1}$$

so that

$$a_\kappa = \frac{a_\kappa + ic_\kappa}{\sqrt{2}}, \qquad \gamma_\kappa = \frac{a_\kappa - ic_\kappa}{\sqrt{2}}. \tag{5.2}$$

One sees from (5.1) and (2.1) that

$$a_{-\kappa} = a_\kappa^\dagger, \qquad c_{-\kappa} = c_\kappa^\dagger. \tag{5.3}$$

The commutation rules satisfied by a's and c's are found by means of (2.3) and (5.1). They are

$$\begin{aligned} a_\kappa a_\mu + a_\mu a_\kappa &= \delta_{\mu,-\kappa}, \\ c_\kappa c_\mu + c_\mu c_\kappa &= \delta_{\mu,-\kappa}, \\ a_\kappa c_\mu + c_\mu a_\kappa &= 0, \end{aligned} \tag{5.4}$$

for $\kappa, \mu = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}, \cdots$. Introducing the operators

$$\begin{aligned} \mathrm{L}_\kappa &= a_\kappa^\dagger a_\kappa = a_{-\kappa} a_\kappa, \\ \kappa > 0 \qquad \mathrm{N}_\kappa &= c^\dagger{}_\kappa c_\kappa = c_{-\kappa} c_\kappa, \end{aligned} \tag{5.5}$$

one has as in I

$$\begin{aligned} \mathrm{L}_\kappa + \mathrm{N}_\kappa &= \mathrm{N}_\kappa^{(+)} + \mathrm{N}_\kappa^{(-)}, \\ \kappa > 0 \qquad \mathrm{L}_\kappa - \mathrm{N}_\kappa &= a_\kappa^\dagger \gamma_\kappa + \gamma_\kappa^\dagger a_\kappa, \end{aligned} \tag{5.6}$$

so that the expectation value

$$\kappa > 0 \qquad \mathrm{L}_\kappa - \bar{\mathrm{N}}_\kappa = 0, \tag{5.7}$$

from which we can conclude that $\sum_{\kappa > 0} \mathrm{L}_\kappa$ and $\sum_{\kappa > 0} \mathrm{N}_\kappa$ are convergent if we assume that all states above a certain state K are unoccupied, *i.e.*,

$$\mathrm{N}_\kappa^{(+)} = 0, \ \mathrm{N}_\kappa^{(-)} = 0 \text{ for } \kappa > \mathrm{K}. \tag{5.8}$$

6. The Photon Operators and Their Commutation Rules.

As in I, the photon operator is defined by

$$b_k = \frac{i}{\sqrt{|k|}} \sum_{\kappa=-\infty}^{\infty} a_\kappa c_{k-\kappa}, \tag{6.1}$$

for $k = \pm 1, \pm 2, \pm 3, \cdots$.

One may note that

$$b_k^\dagger = b_{-k}. \tag{6.2}$$

It can be demonstrated with the necessary assumptions pointed out in I that

$$\begin{aligned} b_k b_j - b_j b_k &= 0 \quad \text{if } k + j \neq 0, \\ b_k b_{-k} - b_{-k} b_k &= 1 \quad \text{if } k > 0. \end{aligned} \tag{6.3}$$

The various other forms of b_k are

$$b_k = -\frac{1}{\sqrt{|k|}} \sum_{\kappa=-\infty}^{\infty} a_\kappa \gamma_{k-\kappa},$$

$$b_k = -\frac{1}{\sqrt{|k|}} \sum_{\kappa=-\infty}^{\infty} a_\kappa a^\dagger{}_{-k},$$

$$b_k = -\frac{1}{\sqrt{|k|}} \left\{ \sum_{\kappa=\frac{1}{2}}^{k-\frac{1}{2}} a_\kappa \gamma_{k-\kappa} + \sum_{\kappa=\frac{1}{2}}^{\infty} (a_{k+\kappa} a_\kappa^\dagger - \gamma_{k+\kappa} \gamma_\kappa^\dagger) \right\}. \tag{6.4}$$

7. The Operator B and Its Properties.

If we define the operator B as

$$\mathrm{B} = i \sum_{-\infty}^{\infty} a_\kappa \, c_{-\kappa}, \tag{7.1}$$

it can be found as in I that

$$\begin{aligned} \mathrm{B} &= \sum_{\frac{1}{2}}^{\infty} (a_\kappa^\dagger \, a_\kappa - \gamma_\kappa^\dagger \, \gamma_\kappa), \\ &= \sum_{\frac{1}{2}}^{\infty} (\mathrm{N}_\kappa^{(+)} - \mathrm{N}_\kappa^{(-)}), \end{aligned} \tag{7.2}$$

and that it has whole number eigen-values. As in I, we note that B commutes with all b_k, *i.e.*,

$$\mathrm{B}\, b_k - b_k \, \mathrm{B} = 0. \tag{7.3}$$

8. Photons and Their Statistical Equilibrium with Matter.

For a state with given numbers of neutrinos and anti-neutrinos the operator representing the number of photons in the kth energy state is not a diagonal matrix. But we can calculate its average value or expectation value—the diagonal element of P_k :

$$\begin{aligned} \mathrm{P}_k \, (t_{1/2}, t_{-1/2}, t_{3/2}, t_{-3/2}, - - -) &= (b_k^\dagger \, b_k) \, (t_{1/2}, t_{-1/2}, - - - -) \\ &= (b_k^\dagger \, b_k) \, (- -, t, - -) \\ &= \sum_{--, t', --} | \, b_k \, (- -, t', - - ; - -, t, - -) \, |^2. \end{aligned} \tag{8.1}$$

We find from (6.4) that

$$\begin{aligned} &| \, b_k \, (- -, t', - - ; \; - -, t, - -,) \, | = \\ &\quad \frac{1}{\sqrt{|\, k \,|}} \left\{ \Big| \sum_{\frac{1}{2}}^{k - \frac{1}{2}} (a_\kappa \, \gamma_{k-\kappa}) \, (- -, t', - - ; - -, t, - -) \right. \\ &\qquad\qquad \left. + - - + - - \Big| \right\}, \\ &= \frac{1}{\sqrt{|\, k \,|}} \left\{ \Big| \sum_{\frac{1}{2}}^{k - \frac{1}{2}} a_\kappa \, (- -, t', - - ; - -, t'', - -) \, \gamma_{k-\kappa} \; (- -, t'', - - ; \right. \\ &\qquad\qquad \left. - -, t, - -) + - - + - - \Big| \right\}. \end{aligned} \tag{8.2}$$

We know from (4.2) that the non-vanishing elements of a_κ are those for which $t'_\kappa \to t''_\kappa$ is $0 \to 1$ or $0 \to \bar{1}$ whereas other t's are unchanged. The elements of $\gamma_{k-\kappa}$ which do not vanish are those for which $t''_{k-\kappa} \to t_{k-\kappa}$ is $0 \to 1$ or $0 \to \bar{1}$, other t's unchanged. Thus the elements of $a_\kappa \, \gamma_{k-\kappa}$ do not vanish if all t'''s are equal to the corresponding t'''s and t's *except*

$$\begin{aligned} t''_\kappa &= t_\kappa = 1 \text{ or } \bar{1}, \\ t'_\kappa &= 0 \text{ or } \bar{0} \, ; \end{aligned} \tag{8.3}$$

and

$$t'_{k-\kappa} = t''_{k-\kappa} = 0 \text{ or } \bar{0},$$
$$t_{k-\kappa} = 1 \text{ or } \bar{1}.$$

Thus the elements of $a_\kappa\ \gamma_{k-\kappa}$ do not vanish only when $(t_\kappa, t_{k-\kappa})$ assumes the values (1, 1), ($\bar{1}$, $\bar{1}$), (1, $\bar{1}$) and ($\bar{1}$, 1) respectively. *In the first two combinations there is no change in the spin states between the absorbed and the emitted neutrinos while in the remaining two combinations the spin states are opposite.** If t_κ is 1 the probabilities that $t_{k-\kappa}$ is 1 or $\bar{1}$ are equal. From this we conclude that the contribution to $\bar{P}_k$ by the matrix $a_\kappa\ \gamma_{k-\kappa}$ is

$$\frac{1}{2k}\, N_\kappa^{(+)}\, N_{k-\kappa}^{(-)} \tag{8.4}$$

As in I, $\bar{P}_k$ can be written as

$$\bar{P}_k = \frac{1}{2k} \sum_{\frac{1}{2}}^{k-\frac{1}{2}} N_\kappa^{(+)}\, N_{k-\kappa}^{(-)} + \frac{1}{2k} \sum_{\frac{1}{2}}^{\infty} \{N_{k+\kappa}^{(+)}\,(1 - N_\kappa^{(+)}) + N_{k+\kappa}^{(-)}\,(1 - N_\kappa^{(-)})\}$$

One may note, however, that the maximum value of N_κ is *two* instead of *one* in the old theory. In considering the statistical equilibrium between matter and radiation, we assume that the average number of particles in the (1, 1) state of $a_\kappa^\dagger\ a_\kappa$ given by (4.1) is equal to the number of particles in the ($\bar{1}$, $\bar{1}$) state of $a_\kappa^\dagger\ a_\kappa$. That is,

$$N_\kappa^{(+)}\,(1, 1) = N_\kappa^{(+)}\,(\bar{1}, \bar{1}),$$
$$N_\kappa^{(-)}\,(1, 1) = N_\kappa^{(-)}\,(\bar{1}, \bar{1}). \tag{8.6}$$

Replacing k in (8.5) by l so that there may not be any confusion between it and the Boltzmann constant, we can show as in I that

$$N_l^{(+)}\,(1, 1) = N_l^{(+)}\,(\bar{1}, \bar{1}) = \frac{ay}{1 + ay}$$
$$N_l^{(-)}\,(1, 1) = N_l^{(-)}\,(\bar{1}, \bar{1}) = \frac{y/a}{1 + y/a} \tag{8.7}$$

where $y = \exp(-\beta l)$ and $\beta = h\nu_1/kT$, k being the Boltzmann constant. Putting

and

$$\kappa = l\ \omega,$$
$$\nu_1 l = \nu, \tag{8.8}$$

we have

$$\exp(-\beta\kappa) = y^\omega \tag{8.9}$$

and

$$d\kappa = l\ d\omega. \tag{8.10}$$

---

* These considerations are the same as put forward earlier by the help of two dimensional matrix representations. Indeed, $b_{k,\rho}$ corresponded to the case of the same spin between the emitted and absorbed particles while $b_{k,\lambda}$ corresponded to the case of opposite spin between them (reference 8).

Replacing the sum by integrals

$$\overline{P(\nu)} = 2\int_0^1 \frac{ay^\omega}{1+ay^\omega}\cdot\frac{{}^1/_a\, y^{1-\omega}}{1+{}^1/_a\, y^{1-\omega}}\,d\omega + \int_0^\infty \frac{ay^{1+\omega}}{(1+ay^{1+\omega})}\cdot\frac{1}{(1+ay^\omega)}\,d\omega$$
$$+\int_0^\infty \frac{{}^1/_a\, y^{1+\omega}}{1+{}^1/_a\, y^{1+\omega}}\cdot\frac{1}{1+{}^1/_a\, y^{1+\omega}}\,d\omega.$$

If we substitute $(1-z)/z$ for ay^ω in the first integral, for $ay^{1+\omega}$ in the second integral and ${}^1/_a\, y^{1+\omega}$ in the third integral, we get

$$P(\nu) = \frac{2y}{1-y} \tag{8.12}$$

As in I, we can also show that

$$P(\nu) = 2\int_{-\infty}^{\infty}\frac{ay^\omega}{(1+ay^\omega)}\left(1-\frac{ay^{\omega-1}}{1+ay^{\omega-1}}\right)d\omega$$
$$= \tfrac{1}{2}\sum_{-\infty}^{\infty} N_\kappa\,(1-N_{\kappa-l}) \text{ where } \nu = l\nu_1. \tag{8.13}$$

Since $y = \exp(-h\nu/kT)$, we get

$$P(\nu) = \frac{2}{\exp(h\nu/kT)-1}. \tag{8.14}$$

The factor 2 in (8.14) distinguishes this formula from the corresponding one in I. It expresses the fact that there are two independent states of different polarisation for a photon with a given frequency. The presence of this factor is necessary to get Planck's formula with the correct factor. Assuming that (8.14) holds also in the case of three dimensions which case has been treated by Jordan and Kronig, one gets Planck's formula by multiplying (8.14) by the individual energy $h\nu$ of the photons having a frequency between ν and $\nu+d\nu$ and by their number $4\pi\nu^2 d\nu/c^3$,

$$\frac{8\pi\nu^2 d\nu}{c^3}\,\frac{h\nu}{\exp(h\nu/kT)-1}. \tag{8.15}$$

10. The Relation between the Energy of Neutrinos and Photons.

Just as in I, the energy of the neutrino field

$$E = \sum_{\kappa=\frac{1}{2}}^{\infty}\kappa\,(L_\kappa + N_\kappa) = \sum_{\kappa=\frac{1}{2}}^{\infty}\kappa\,(N_\kappa^{(+)} + N_\kappa^{(-)}) \tag{9.1}$$

and the energy of the photon field

$$W = \sum_{k=1}^{\infty} k\,P_k = \sum_{k=1}^{\infty} k\,b_k^\dagger\,b_k \tag{9.2}$$

have the following relation

$$E - W = B^2/2. \tag{9.3}$$

The proof of this relation due to Kronig, is contained in I which holds here also.

AN OPTICAL INVESTIGATION OF SOME INDIAN OILS.

III. Intensity of the Scattered Light.

By Ch. V. Jogarao.

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(Communicated by Mr. S. Bhagavantam.)

1. *Introduction.*

In an earlier paper in this Journal (Jogarao, 1936) the results of a study of the depolarisation of the transversely scattered light in a number of oils have been reported. In the present paper the same oils have been studied in respect of the intensity of the scattered light. Such an investigation, besides furnishing us valuable information regarding the optical characters of the oils, is expected to decide whether the scattered beam observed in these oils has a genuine molecular origin or is due to any other kind of phenomenon. The two most important factors that make the scattered light appear more intense than what it really ought to be are fluorescent impurities and dust particles in the scattering liquid. These two disturbing factors are eliminated in the following manner.

2. *Eliminating Dust Particles and Fluorescence.*

It has already been mentioned that these oils could not be distilled even in vacuum without decomposition. As such, a systematic process of refining described in the first paper of this series has been applied to each one of the oils studied. As has been done in the paper already referred to, effects due to fluorescence are avoided by interposing a deep red glass in the path of the incident beam before obtaining the estimates of the intensity of the scattered beam. Dust could not be removed by the above process but considerable success in this direction was attained by continuously centrifuging the oil so purified for a number of hours in an Ecko centrifuge (3600 R.P.M.). A series of observations given below in the case of olive oil clearly show the effect of continued centrifuging. The intensity of the scattered light gradually decreased until it attained an almost steady value after about seven hours of centrifuging.

Time of centrifuging	Fresh	2 hrs.	6 hrs.	7 hrs.	7½ hrs.
Relative Intensity of scattered light (Ether=1)	4·8	2·7	1·86	1·8	1·8

In this manner all the oils studied have been rendered practically dust-free and fit for optical investigation. The depolarisation factors for the oils have been re-measured in the present investigation and the values obtained now are not very different from the values obtained before. It may be noted here that in the former investigation, the track of the scattered light in gingelly oil was found to be reddish. The gingelly oil has been centrifuged in the manner described above in the present investigation and the scattered light in this sample is found to exhibit a rich blue colour. It has also been noticed in the earlier paper that the scattered beam in gingelly oil is different from the other oils in that it showed a value of 0·7 for ρ_h and as the track was reddish much significance was not attached to this result. In the present investigation, the track is found to exhibit a value of 1 for ρ_h in conformity with the other oils.

3. *Experimental Arrangements.*

The intensity of the scattered light (Ether = 1 ; Benzene = 3·2) has been measured by means of the rotating sector photometer, constructed in this laboratory. Benzene has been taken as the standard. Pure redistilled benzene and the purified and dust-free oil are contained in two cubical glass cells. The glass cells are covered with black paper on the outside excepting windows for the passage of incident light and the observation of the scattered light. The openings are kept so that the scattered beams emerge out of the two cells side by side. Light from a carbon arc is focussed by means of a Zeiss biotar lens fixed in the side of the dark cabin, into the cells. The path of the beam through the cells has been adjusted to be narrow and parallel.

The sector photometer has been made as follows. A brass circular disc 1/16″ thick and 6½″ diameter, having a sector of 60° opened in it has been mounted coaxially along with another similar brass disc of radius 5½″ but having a suitable opening. The two are attached to a pulley with ball bearings, so that the whole can be rotated in a vertical plane at a very high speed by means of an electric motor.

The glass cells are mounted behind the sector at the same height. The intensities are compared in the usual manner.

At first the oils showed much greater intensity than benzene even when a deep red glass has been interposed into the path of the incident beam but

the intensity soon became much less on purification by centrifuging. The results are given in the following table.

Intensity of Transversely Scattered Light in Oils.

Oil	Intensity of the scattered light (Ether=1) with a deep red glass interposed	Depolarisation $\rho \times 100$	
		Revised values	Old values
Castor oil ..	1·92	40·1	46·0
Olive oil ..	1·80	27·0	20·9
Cocoanut oil ..	2·40	39·2	42·2
Groundnut oil ..	2·24	34·0	35·5
Gingelly oil ..	2·52	11·7	12·7

The depolarisation values obtained with the oils after intense centrifuging are given here for comparison along with the values obtained previously.

4. Comparison with Theory.

The following formula* gives us a method of calculating the relative intensities of the transversely scattered light.

$$\frac{I}{I_0} = \frac{\pi^2}{2d^2} \cdot \frac{RT\beta}{N\lambda^4} \cdot (\mu^2 - 1)^2 \frac{6 + 6\rho}{6 - 7\rho}.$$

The various letters have the usual significance. If I_1 and I_2 represent the intensities of light scattered by two liquids for identical values of I_0, λ and T, we have

$$\frac{I_1}{I_2} = \frac{(\mu_1^2 - 1)^2}{(\mu_2^2 - 1)^2} \cdot \frac{\beta_1}{\beta_2} \cdot \frac{6 + 6\rho_1}{6 + 6\rho_2} \cdot \frac{6 - 7\rho_2}{6 - 7\rho_1}.$$

Compressibility values are available only for castor and olive oils. So the relative values of the intensity of the scattered light (Ether = 1; Benzene = 3·2) in the case of these two oils is calculated and given in the following table, along with the values obtained experimentally.

* See J. Cabannes, *La Diffusion Moleculaire de La Lumiere*, 1929, p. 236.

Oil	Refractive Index (Jogarao, *loc. cit.*)	Compressibility (*I.C.T.*, Vol. II)	Depolarisation	Intensity (Calc.) (Ether = 1)	Intensity (Obs.) (Ether = 1)
Castor oil	1·47763	47	·40	1·66	1·92
Olive oil	1·46807	56	·27	1·38	1·80

Data regarding the compressibilities of the other oils are not available and as such a comparison with theory in those cases is not possible. A systematic study of the compressibilities of oils, however, is in progress in this laboratory and use will be made of the values as soon as they are available. It may be concluded that there is satisfactory agreement between the calculated and observed values of the intensity of the transversely scattered light in the case of castor and olive oils. This result establishes the fact, that, provided care has been taken to eliminate fluorescence by interposing a deep red glass and dust by powerful and continued centrifuging, the oils exhibit a scattered beam having a genuine molecular origin and hence subject to the usual laws of molecular scattering in dense media.

5. *Summary.*

The intensity of the transversely scattered light (Ether = 1 ; Benzene = 3·2) in the case of five dust-free oils is measured by means of the rotating sector photometer. Using values of compressibility, refractive index and depolarisation available for olive and castor oils, the intensity of the scattered light is calculated. The calculated values agree with the experimental values. It is concluded that the light scattered by the oils is molecular in origin.

The author takes this opportunity of thanking Mr. S. Bhagavantam, the Head of the Physics Department, for his kind guidance during the course of the work.

REFERENCE.

Jogarao, Ch. V., *Proc. Ind. Acad. Sci.*, 1936, **4**, 327.

ON A CONJECTURE OF RAMANUJAN.

By Hansraj Gupta.
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Received September 10, 1936.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

By using the Hardy-Ramanujan asymptotic formula for $p(n)$—the number of unrestricted partitions of n, true for large values of n, Lehmer[1] has recently found that

$$(1)\quad p(599) = 4353\ 50207\ 84031\ 73482\ 70000$$
$$\equiv 0 \pmod{5^4};$$

and

$$(2)\quad p(721) = 16\ 10617\ 55750\ 27947\ 76355\ 34762$$
$$\equiv 0 \pmod{11^3}.$$

In a foot-note, however, Lehmer expresses a doubt with regard to the exactness of these values. He states that the value given in (1) is either correct or differs from the true value of $p(599)$ by a multiple of 125. Similar remarks apply to (2). If the second alternative were true, it would not necessarily follow that

$$p(599) \equiv 0 \pmod{5^4},$$

or that

$$p(721) \equiv 0 \pmod{11^3};$$

and the object of Lehmer's note would be defeated.

I have recently extended my table[2] for $p(n)$ to $n \leqslant 600$. I find that the value of $p(599)$ obtained by Lehmer is absolutely correct. From the tables appended to this note, it appears that the value of $p(721)$ given by him is also correct.

Tables I and II give the values of i and j,

where $p(n) \equiv i \pmod{13}$,

and $\equiv j \pmod{19}$;

for the values $0 \leqslant n \leqslant 721$.

The numbers i and j being small are very easy to handle. The actual extension of the table of partitions involves a lot of labour. The method[3] employed in the calculation of the tables for i and j, is the same as that for the calculation of the table of partitions, but the labour involved is very much less. Besides this, these tables provided simple checks on the values of $p(n)$ as the work of computation proceeded. The part of Table I, beyond

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[1] D. H. Lehmer, "On a Conjecture of Ramanujan," *Jour. London Math. Soc.*, 1936, **11**, 114–118.

[2] This extension is to appear in the *Proc. London Math. Society*.

[3] H. Gupta, "A Table of Partitions," *Proc. London Math. Soc.*, 1935, **39**, (2), 142–149. See section 5 in particular.

$n = 600$, and the latter half of Table II, have been calulated by my younger brother and pupil Dinanath Gupta. It will not be out of place to state that in order to find whether or not $p(t) \equiv 0 \pmod{s}$, all that is necessary is to prepare a similar table modulo s.

TABLE I.

n	0	1	2	3	4	5	6	7	8	9
0	1	1	2	3	5	7	11	2	9	4
1	3	4	12	10	5	7	10	11	8	9
2	3	12	1	7	2	8	5	7	0	2
3	1	4	3	3	12	11	11	5	2	11
4	2	6	4	3	9	6	11	6	9	1
5	9	2	9	4	3	7	11	8	12	2
6	8	8	0	8	7	2	4	12	1	2
7	1	6	6	3	2	11	6	7	5	10
8	7	3	3	11	0	12	6	6	6	5
9	11	12	8	2	0	2	9	1	10	9
10	4	2	4	11	11	11	2	8	6	4
11	7	5	5	11	7	6	8	4	4	12
12	1	9	10	11	9	8	11	3	11	0
13	9	1	10	1	3	7	0	3	3	10
14	9	4	7	2	10	9	10	2	9	4
15	7	12	3	2	7	4	12	4	11	2
16	1	10	10	6	11	10	6	1	8	2
17	7	5	6	0	1	11	10	10	11	4
18	0	4	5	5	7	4	8	10	4	7
19	10	5	6	6	9	9	12	0	11	6
20	12	2	2	8	6	4	2	10	7	4
21	6	2	3	0	11	12	10	1	2	0
22	7	1	3	12	11	2	0	0	4	9
23	12	1	5	8	1	6	12	0	5	11
24	0	8	3	10	9	5	4	11	4	2
25	9	7	12	3	5	11	3	10	4	7
26	7	11	7	7	0	12	1	2	10	8
27	8	11	6	4	10	5	2	10	11	7
28	7	10	10	2	10	7	11	10	3	6
29	12	4	2	10	0	7	5	7	9	3
30	2	10	7	8	8	5	1	4	1	4
31	7	0	7	8	5	1	7	4	0	5
32	2	1	2	11	1	4	0	10	9	5
33	6	4	9	3	6	0	8	4	0	8
34	4	9	1	11	4	6	3	2	4	2
35	1	12	2	2	4	7	8	0	0	12

TABLE I—(*contd.*)

n	0	1	2	3	4	5	6	7	8	9
36	8	11	9	11	3	6	9	3	1	4
37	3	4	7	2	9	7	4	6	2	3
38	1	11	8	7	11	9	3	12	12	0
39	8	6	7	2	11	4	1	9	10	5
40	8	4	10	12	3	10	5	10	10	10
41	5	2	2	9	9	1	6	4	0	9
42	12	5	3	5	9	1	10	4	3	4
43	7	6	8	11	2	12	9	9	7	5
44	12	3	8	10	1	12	7	5	1	1
45	3	8	4	0	5	10	1	2	0	5
46	11	5	8	12	1	5	1	4	2	11
47	5	5	10	0	12	2	12	7	12	11
48	2	8	0	10	0	9	0	5	9	5
49	2	6	9	6	1	1	1	11	7	2
50	12	2	7	3	6	6	9	5	0	6
51	8	3	10	9	11	12	8	7	3	12
52	4	12	4	12	11	5	5	2	7	0
53	8	12	1	5	11	2	10	7	0	5
54	12	3	0	4	8	9	2	6	10	7
55	8	5	9	1	5	4	5	2	9	1
56	9	11	0	11	7	1	6	12	3	9
57	11	3	4	5	9	3	12	8	7	1
58	6	3	4	4	8	3	10	8	6	10
59	6	1	3	10	1	8	10	4	5	10
60	0	9	5	12	11	7	3	6	11	4
61	12	11	11	5	2	6	4	3	11	9
62	12	11	3	7	5	10	8	2	12	7
63	11	7	8	5	12	0	6	11	1	3
64	7	3	9	9	0	8	2	11	3	10
65	11	9	5	8	1	4	4	1	2	9
66	6	11	1	10	3	8	4	4	0	12
67	0	3	7	8	1	11	8	10	1	8
68	5	2	6	7	0	9	6	12	6	5
69	4	8	2	10	2	8	2	0	5	0
70	2	3	3	12	7	4	10	1	8	10
71	4	1	1	0	0	5	3	5	11	9
72	8	3	..	..	..	..	..	..	..	..

TABLE II.

n	0	1	2	3	4	5	6	7	8	9
0	1	1	2	3	5	7	11	15	3	11
1	4	18	1	6	2	5	3	12	5	15
2	0	13	14	1	17	1	4	8	13	5
3	18	2	8	16	17	6	3	15	4	6
4	3	9	12	10	11	5	13	0	4	17
5	14	11	9	15	18	7	10	17	3	0
6	13	11	5	15	14	2	10	5	7	15
7	4	6	13	11	11	1	10	3	18	6
8	9	3	11	9	14	12	15	12	8	9
9	18	13	15	2	13	8	6	4	1	10
10	14	6	16	10	2	11	6	2	2	6
11	12	2	1	4	14	13	6	13	5	17
12	9	9	9	12	15	18	18	12	16	3
13	10	15	12	3	13	15	17	15	10	18
14	9	3	13	15	18	15	5	6	17	8
15	12	2	12	4	14	0	17	16	14	3
16	17	5	5	17	7	16	1	0	18	13
17	14	10	12	6	13	17	8	4	7	15
18	12	13	10	11	6	13	3	12	8	17
19	4	10	18	17	13	12	7	17	16	4
20	1	0	10	18	0	8	3	6	2	0
21	14	3	8	15	14	11	17	3	14	14
22	4	9	3	14	8	5	6	13	9	14
23	3	17	1	15	18	5	4	14	16	6
24	5	12	6	9	14	2	15	5	11	16
25	9	1	7	2	8	16	7	18	3	2
26	12	10	0	8	6	2	5	11	2	13
27	14	13	13	10	16	18	10	7	9	10
28	5	17	8	3	11	17	11	9	15	7
29	2	17	13	18	9	3	11	13	7	17
30	17	2	8	11	15	18	12	5	12	11
31	6	18	3	17	16	9	3	6	15	10
32	18	17	11	8	0	9	8	11	10	16
33	7	7	11	8	3	12	5	13	6	16
34	14	1	0	15	3	15	11	15	11	16
35	18	7	11	4	10	17	16	3	4	3

TABLE II—(*contd.*).

n	0	1	2	3	4	5	6	7	8	9
36	8	18	17	2	10	2	7	17	17	14
37	13	6	12	15	13	2	10	1	11	15
38	11	7	6	7	13	17	2	14	7	14
39	15	6	1	16	2	12	9	15	18	14
40	10	4	1	7	13	16	11	18	18	0
41	10	12	4	6	6	6	12	18	2	15
42	14	3	10	11	1	0	3	2	3	15
43	6	8	4	14	0	12	3	7	12	12
44	16	7	16	8	10	15	15	9	16	2
45	9	15	3	10	9	15	15	13	14	10
46	10	0	18	8	4	0	14	4	10	0
47	0	3	0	5	17	12	15	9	1	9
48	3	7	5	8	11	6	2	7	4	15
49	1	5	1	3	13	6	14	13	10	4
50	18	5	15	9	13	14	15	9	17	14
51	0	14	4	1	17	16	0	9	17	9
52	16	12	12	15	1	17	0	5	9	5
53	14	13	7	7	4	2	15	17	7	13
54	1	9	3	2	0	1	8	0	15	7
55	9	18	4	18	18	12	14	12	9	12
56	11	10	5	11	3	17	2	13	15	12
57	13	14	2	3	18	0	17	11	7	3
58	14	2	16	0	7	0	9	9	17	12
59	9	15	13	12	4	0	8	14	15	2
60	18	15	4	3	9	16	12	16	15	12
61	12	13	17	18	0	9	0	8	14	4
62	13	14	3	7	18	11	14	18	3	16
63	11	5	3	3	6	12	4	8	6	4
64	5	12	6	4	4	9	13	7	16	14
65	16	6	11	15	3	5	7	12	5	16
66	4	12	4	5	2	10	4	4	7	0
67	13	5	7	4	13	0	1	6	6	11
68	13	7	9	11	11	15	17	2	15	18
69	2	3	5	7	6	17	5	16	11	4
70	18	7	11	6	9	18	6	17	2	11
71	3	9	7	4	5	4	16	5	17	10
72	16	18	..	..	..	..	..	..	..	..

REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED α-β UNSATURATED CARBONYL COMPOUNDS.

Part III. Action of Mercuric Acetate on Coumarinic and Coumaric Acids and Esters.

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and
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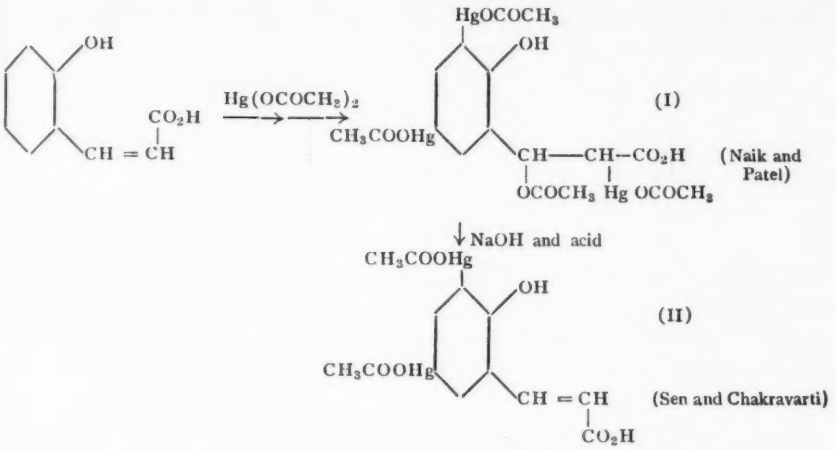
Received November 2, 1936.

It was shown in Part II[1] that when mercuric acetate reacts with coumarin, 7-methyl and 6-nitrocoumarins in alcoholic solution addition at the double bond takes place and along with this mercuration is effected in positions 6 and 8 if they should be free. Sen and Chakravarti[2] and Naik and Patel[3] who failed to observe this opened out the pyrone ring by dissolving coumarin in aqueous alkali and after neutralising the excess of alkali added to it mercuric acetate. The product was considered to be diacetoxymercuri-coumaric acid by the former authors whereas the latter thought it was bisacetoxymercuri-coumarin. We[4] have already shown that it is a coumaric acid derivative and not a coumarin. Although due to the inherent defect of the method and the sparing solubility of the product in ordinary solvents it is not possible to obtain it as pure as desirable, the differences between the analytical figures for mercury of the two groups of authors is more than what can be expected from such considerations. On closer scrutiny we realised that there was a slight difference between the two methods. Sen and Chakravarti purified their product by dissolving it in caustic alkali and reprecipitating it with acetic acid whereas Naik and Patel seem to have omitted this step. By making this distinction we have been able to reproduce the results of both groups of authors and we suggest that the following represents correctly the course of reaction.



The triacetoxymercuri compound (α : 3 : 5-triacetoxymercuri-β-acetoxy melilotic acid) resulting from addition at the double bond and simultaneous mercuration is produced first and this eliminates the addenda on treatment with alkali and goes over into the diacetoxymercuri-coumaric acid on acidification. This satisfactorily explains our results and the results of older investigators as shown below :

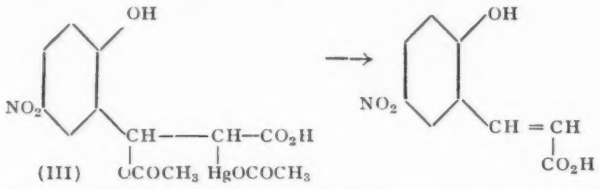
Required for formula I : Hg, 60·2% ; Found : by Naik and Patel, 60·8% ; by us 60·6%.

Required for formula II : Hg, 58·9% ; Found : by Sen and Chakravarti, 58·4% ; by us, 58·4%.

In support of the above explanation may be stated the following points: (1) mercury salts have been shown to add on to the double bond in coumarins and acids derived from them (see Part II[1] and this paper also) ; (2) the elimination of the addenda takes place in alkaline solution in the case of coumarin-mercuri-chloride, β-methoxymelilotic acid (see Part II) and melilotic acid-β-sulphonate (Dey and Row[5]).

The position is slightly different in the case of 6-nitrocoumarin. Under the above conditions the nitrocoumarinic acid forms a mono-mercuri compound which eliminates the mercury completely on simple solution in aqueous alkali so that subsequent acidification with acetic acid or hydrochloric acid yields free nitrocoumaric acid (see Sen and Chakravarti[2] also). Mercury analysis of the mercury compound shows that it is an addition product of 5-nitrocoumarinic acid and mercuric acetate and the constitution III (α-acetoxymercuri-β-acetoxy-5-nitro-melilotic acid) explains the ready

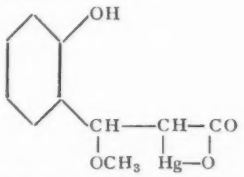
elimination of mercury since compounds mercurated in the benzene nucleus do not eliminate mercury under such conditions.



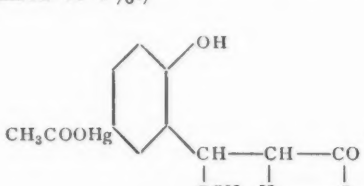
(III)

Obviously in the reaction of mercuric acetate under mild conditions the nitro group is able effectively to prevent the mercuration of the benzene ring so that addition at the double bond alone takes place. It may therefore be stated that the addition reaction takes place with great facility in the case of these acids.

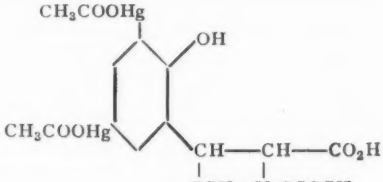
The action of mercuric acetate on coumaric acid in cold methyl alcoholic solution was first studied by Biilmann[6] who assigned the following constitution to the product as an inner anhydride.



At the temperature of our laboratories (30° C.) we could not reproduce the result since the product contained a higher percentage of mercury and did not seem to have a definite composition. At the boiling point of methyl alcohol, however, a definite product was obtained with very great ease. On the basis of the inner anhydride formulation of Biilmann the mercury analysis indicated that this product had the constitution (IV). (Found: Hg, 61·5%. Required for formula IV 61·4%.) But it was easily soluble in aqueous sodium bicarbonate thereby showing that it had a free carboxyl group. The mercury percentage is also compatible with the alternative formula (V). (Required 61·9%.)

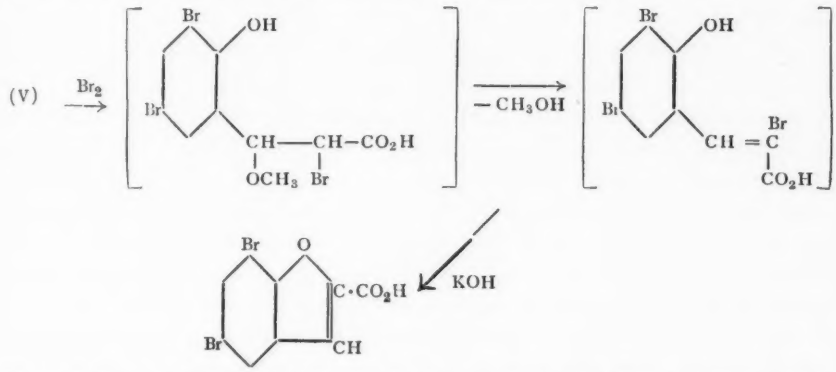


(IV)



(V)

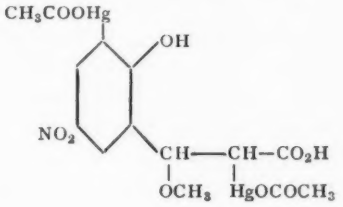
That the latter formula is the correct one is shown by the following facts: (1) the compound is easily soluble in cold aqueous sodium bicarbonate; (2) the percentage of carbon in it agrees with this formula. (Found: C, 20·3%; Formula IV required 22·0% and Formula V required 19·8%); (3) in the presence of glacial acetic acid it reacts rapidly with bromine producing mercuric bromide and a bromocompound which on treatment with alcoholic potash gives 4 : 6-dibromocoumarilic acid (Simonis and Wenzel[7]).



Hence it has to be concluded that in boiling methyl alcoholic solution mercuric acetate not only adds on to the double bond in coumaric acid but also mercurates positions *para* and *ortho* to the hydroxyl group and that the product does not possess the anhydride formula. When dissolved in sodium hydroxide and decomposed with hydrogen sulphide it forms β-methoxy-melilotic acid.

The methyl ester of coumaric acid reacts with mercuric acetate in methyl alcoholic solution giving the methyl ester of compound (V) containing three atoms of mercury. It is insoluble in aqueous sodium carbonate. It reacts rather more easily than the acid with bromine giving a bromocompound which eventually gives 4 : 6-dibromocoumarilic acid when treated with alcoholic potash.

5-nitrocoumaric acid forms a dimercury compound which is obviously a : 3-diacetoxymercuri-5-nitro-β-methoxy-melilotic acid.



(VI)

With aqueous potash and hydrogen sulphide it formed 5-nitro-coumaric acid owing to the instability of the corresponding nitro-methoxy-melilotic acid. With bromine it formed a bromocompound which with boiling aqueous potash gave 6-bromo-4-nitrocoumarilic acid identified by comparison with a specimen obtained from 3 : 8-dibromo-6-nitro-coumarin (Dey and Row[5]).

The methyl ester of the nitro-coumaric acid behaved quite similarly giving rise to products which eventually gave the above bromo-nitrocoumarilic acid.

The series of reactions outlined above have again been achieved with 4-methyl-coumaric acid and its methyl ester. They form 3 : 5 : α-triacetoxymercuri-4-methyl-β-methoxy melilotic acid and its methyl ester respectively. The bromocompounds obtained from these give with alcoholic potash 4 : 6-dibromo-5-methyl-coumarilic acid identical with the one obtained from 7-methyl-3 : 6 : 8-tribromocoumarin (see Part II[1]).

Experimental.

Action of Mercuric Acetate in Aqueous Solution.

(i) *On coumaric acid* : 3 : 5 : *α-triacetoxymercuri-β-acetoxy melilotic acid.*—Coumarin (2 g.) was dissolved in 1% aqueous sodium hydroxide (220 c.c.), the cold solution was neutralised with acetic acid (litmus) and immediately treated with a cold aqueous solution of mercuric acetate containing a little acetic acid (13 g. of mercuric acetate in 100 c.c. of water). On shaking the mixture a bulky flocculent precipitate separated out. It was filtered and washed thoroughly with very dilute cold acetic acid till the wash liquid gave no test for mercury and finally with about 200 c.c. of hot alcohol. The substance was dried first in air and finally in a vacuum desiccator. The yield was 6 g. The compound did not exhibit any definite crystalline structure and was sparingly soluble in all the ordinary organic solvents. It was, however, easily soluble in aqueous sodium carbonate and bicarbonate and decomposed on heating at 245°. (Found : Hg, 60·6 ; $C_{17}H_{18}O_{11}Hg_3$ required Hg, 60·2%.) (Compare Naik and Patel[3].)

3 : 5-*diacetoxymercuri-coumaric acid.*—The above compound was treated with aqueous sodium hydroxide, filtered and the clear filtrate acidified with acetic acid. The white precipitate that was produced was filtered and washed thoroughly first with cold water containing acetic acid and finally with alcohol. It exhibits no definite crystalline structure, is sparingly soluble in ordinary organic solvents, dissolves easily in aqueous sodium bicarbonate and decomposes at 215° C. (Found : Hg, 58·4 ; $C_{13}H_{12}O_7Hg_2$ required Hg, 58·9%.) (Compare Sen and Chakravarti[2].) The two compounds

described above yielded coumaric acid on being decomposed with hydrogen sulphide in alkaline solution.

(ii) *On 5-nitrocoumarinic acid : 5-nitro-α-acetoxymercuri-β-acetoxymelilotic acid.*—Starting with 6-nitrocoumarin (2 g.) and mercuric acetate (4 g.) the reaction was carried out under the same conditions as with coumarin. The purified dry product decomposed at 170° and weighed 4·5 g. (Found : Hg, 38·2 ; $C_{13}H_{13}O_9NHg$ required Hg, 38·0%.) When the compound was treated with aqueous sodium hydroxide, filtered and the clear filtrate acidified with hydrochloric acid (see Sen and Chakravarti[2]) or even with acetic acid pure 5-nitrocoumaric acid was obtained.

Action of Mercuric Acetate in Methyl Alcoholic Solution.

(i) *On coumaric acid: 3 : 5 : α-triacetoxymercuri-β-methoxymelilotic acid.*—Mercuric acetate (12 g.) was dissolved in pure methyl alcohol (240 c.c.) containing a little acetic acid and a solution of coumaric acid (2 g.) in the same solvent (5 c.c.) added. The mixture which was quite clear in the cold was boiled under reflux. In about 15 minutes a heavy colourless precipitate separated out giving rise to violent bumping. It was filtered off in the hot and washed well with cold dilute acetic acid and subsequently with hot methyl alcohol. Further boiling of the alcoholic solution gave more solid which was however less pure. The yield of the pure dry solid was about 6 g. A better yield could be obtained by using more concentrated solutions but the product was not so pure. It cannot be crystallised from any of the ordinary organic solvents. It is easily soluble in aqueous sodium bicarbonate. The pure substance melts at 234° (decomp.). (Found : Hg, 61·5, C, 20·3 ; $C_{16}H_{18}O_{10}Hg_3$ required Hg, 61·9, C, 19·8%.)

The mercury compound was dissolved in normal sodium hydroxide and was saturated with hydrogen sulphide at 0° C. It was then allowed to stand overnight in the cold chamber, the precipitated mercuric sulphide filtered off and the filtrate kept cooled and acidified with a normal solution of sulphuric acid. Hydrogen sulphide was removed by passing a current of air through the solution. β-methoxy-melilotic acid was thereby obtained as a white solid which was filtered, washed with a small quantity of water and crystallised from hot water, m.p. 125° C. (Compare Part II[1].)

The substance in a fine state of division was suspended in glacial acetic acid and treated with a solution of bromine in the same solvent with vigorous shaking. The colour was rapidly discharged and more bromine was added in small quantities at a time till the colour just persisted after shaking. After filtering off mercuric bromide the acetic acid solution was poured into a large volume of water. The precipitated bromo-compound was crystallised from

ethyl alcohol. The purified product (2 g.) was boiled with alcoholic potash (4 g. in 50 c.c.) for about 3 hours, the solution diluted with water and acidified when a white crystalline solid separated out. It could be recrystallised from glacial acetic acid as colourless long narrow plates melting at 274° and was found to be identical with 4 : 6-dibromo-coumarilic acid prepared directly from 3 : 6 : 8-tribromocoumarin (Simonis and Wenzel[7]).

(ii) *On methyl coumarate.*—The methyl ester of 3 : 5 : α-triacetoxymercuri-β-methoxymelilotic acid was obtained from mercuric acetate and the ester of coumaric acid by the procedure described above. The precipitate was formed after an hour and a half of boiling and the yield of the pure product was 7 g. from 2 g. of coumaric ester and 12 g. of mercuric acetate.[7] It decomposes at 265°. (Found : Hg, 61·5 ; C, 20·1 ; $C_{17}H_{20}O_{10}Hg_3$ required Hg, 61·0, C, 20·6%.) It was insoluble in aqueous sodium bicarbonate. By the action of bromine in glacial acetic acid a bromocompound was obtained which yielded 4 : 6-dibromo-coumarilic acid on treatment with boiling alcoholic potash.

(iii) *On 5-nitrocoumaric acid.*—3 : α-diacetoxymercuri-5-nitro-β-methoxy melilotic acid was obtained from 5-nitrocoumaric acid (2 g.) which was dissolved in methyl alcohol (10 c.c.) and mixed with mercuric acetate (8 g.) in the same solvent (150 c.c.) containing a little acetic acid. The product separated out after boiling for about 5 minutes. It was yellow and was so fine that it could not be filtered under suction. It was therefore centrifuged and was subsequently purified in the usual way. It was very sparingly soluble in all the ordinary organic solvents, but dissolved easily in aqueous sodium bicarbonate. On heating it turns grey at 258° and does not decompose below 300°. (Found : Hg, 53·4 ; $C_{14}H_{15}O_{10}Hg_2N$ required Hg, 52·9%.)

By the action of hydrogen sulphide in the presence of alkali 5-nitrocoumaric acid was regenerated. Bromine in glacial acetic acid gave a bromocompound which on boiling with 10% aqueous potash for two hours produced an acid identified as 6-bromo-4-nitrocoumarilic acid by comparison with a sample obtained from 3 : 8-dibromo-6-nitrocoumarin (Dey and Row[5]). It should be noted that the use of alcoholic potash in this case results in the production of an impure unworkable product and 10% aqueous potash was found to be the most suitable for the purpose. The coumarilic acid melted at 252–53°.

(iv) *On the methyl ester of 5-nitrocoumaric acid.*—The methyl ester of the above mercurated acid (5 g.) was obtained easily from methyl-5-nitrocoumarate (2 g.) and mercuric acetate (7 g.). It shrinks at about 215° and decomposes at 238°. (Found : Hg, 52·5 ; $C_{15}H_{17}O_{10}Hg_2N$ required Hg, 51·9%.)

The bromocompound produced from this yielded 6-bromo-4-nitrocoumarilic acid on treatment with hot aqueous potash.

(v) *On 4-methyl coumaric acid.*—This acid (2 g.) and mercuric acetate (12 g.) produced 3 : 5 : α-triacetoxy-mercuri-4-methyl-β-methoxymelilotic acid (4 g.) melting at 228° (decomp.). (Found : Hg, 61·4 ; $C_{17}H_{20}O_{10}Hg_3$ required Hg, 61·1%.) No methoxy-melilotic acid derivative could be obtained in this case also by the action of alkali and hydrogen sulphide. The bromocompound obtained by the action of bromine on treatment with 25% aqueous potash gave 4 : 6-dibromo-5-methyl coumarilic acid melting at 270° found to be identical with a sample of the acid obtained from 3 : 6 : 8-tribromo-7-methyl coumarin (see Part II). It crystallised from glacial acetic acid in flat needles. (Found : in silver salt Ag, 25·0%; $C_{10}H_5Br_2O_3Ag$ required Ag, 24·5%.)

(vi) *On the methyl ester of 4-methylcoumaric acid.*—This ester (2 g.) and mercuric acetate (11 g.) in methyl alcohol (200 c.c.) gave 6 g. of the pure product. It turned black at about 255° and melted down to a dark liquid at about 284°. (Found : Hg, 60·7 ; $C_{18}H_{22}O_{10}Hg_3$ required Hg, 60·2%.) The bromocompound produced from this gave the same dibromo-methyl-coumarilic acid on treatment with potash as described above.

Summary.

When mercuric acetate reacts with coumarinic acid in cold aqueous solution it adds on to the double bond and mercurates the benzene ring in positions 3 and 5. When the product is dissolved in sodium hydroxide the addenda get eliminated so that 3 : 5-diacetoxymercuri-coumaric acid is produced on acidification. These compounds yield pure coumaric acid on being decomposed with hydrogen sulphide in alkaline solution. 5-Nitrocoumarinic acid adds only at the double bond and does not get mercurated. The product therefore yields the nitrocoumaric acid easily on dissolving in aqueous alkali and subsequently acidifying the solution.

In methyl alcoholic solution mercuric acetate adds on to the double bond in coumaric acids and their esters and mercurates positions 3 and 5 if they should be free. The constitution of these compounds has been established by treatment with bromine in glacial acetic acid and by examination of the action of caustic alkali on the bromocompounds. They give rise to brominated coumarilic acids.

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3. Naik and Patel, *J. C. S.*, 1934, 1043.
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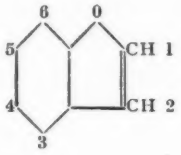
6. Biilmann, *Ann.*, 1912, **388**, 262.
7. Simonis and Wenzel, *Ann.*, 1900, **33**, 421 and 1964.

Note.—The numbering of the positions in the Coumarone ring is that adopted in Richter's Lexicon.



THE CONVECTION AND VARIATION OF TEMPERATURE NEAR A HOT SURFACE.

Part II. Applications of Interferometry to the Measurements of Temperatures and Temperature Gradients Very Close to a Hot Surface.

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1. Introduction.

In Part I of this series[1] a discussion of the dust-free layer or clear space in the neighbourhood of a hot surface was made in the light of a series of experiments with an air cell consisting of a hot surface above and a cold surface below it. It was shown that when these two surfaces were 4 mm. or less apart from each other particles of smoke were repelled from the hot surface to the cold one with a uniform velocity proportional to the temperature gradient. These results indicated a simpler explanation of the formation of the dark layer than that suggested by earlier writers.

In the present paper, we shall first of all describe an interferometric method of measuring temperatures and temperature gradients very close to a hot surface. In a recent note by Ramdas and Paranjpe[2] the importance of making such measurements accurately and the advantages of the interferometric method over the usual methods were briefly indicated. It was pointed out that the insertion of a thermo-couple, or a resistance thermometer, near a hot surface disturbs the isothermal layers of the air near it and vitiate the results. Apart from the inherent difficulties in setting up and handling a sensitive instrument like the interferometer, there are also certain types of deformation of the interference pattern which take place when one of the interfering beams passes through a region with a varying lapse-rate of temperature. It is therefore felt that a full account of the experimental method as well as the special experience gained in the course of the present investigation may be found useful by other workers. After setting out these details we shall discuss the interference patterns and the temperature gradients in the case of thin air cells between a hot surface above and a cold surface below similar to those used in the experiments on the

dark layer (*vide* Part I of this series). The discussion of other interesting cases like (1) the conditions above and below a single hot surface, and (2) above an evaporating surface, etc., will be taken up on a later occasion.

2. *Adjustment of the Interferometer.*

The arrangement of the optical plates and mirrors was essentially that of Mach-Zehnder.[3] A horizontal section of the apparatus is shown in Fig. 1. Light from a sodium vapour lamp S stopped down by a diaphragm D D and rendered parallel by a lens L_1 falls on a plane parallel glass plate P_1, is partially reflected on to the mirror M_2 and after one more reflection at M_2 is transmitted through a parallel plate P_2. We may call this beam A. The beam transmitted by P_1 which we may call B is reflected by the mirror M_1 and the

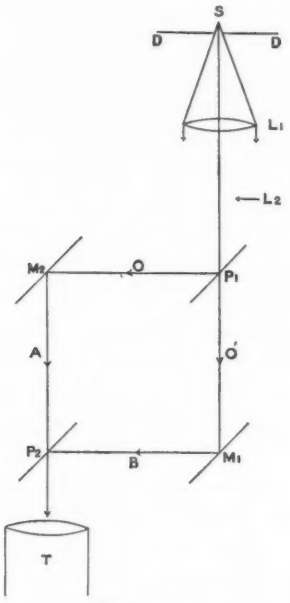

FIG. 1

plate P_2 and then interferes with the other beam. The two beams are seen through a telescope T while adjusting for the interference fringes.

The various movements which can be given to the different mirrors and plates and the details of their adjustments are as follows :—

(i) The plate P_1 can be turned about a vertical axis, but no fine adjustment has been provided.

(ii) The mirror M_1 is mounted on a platform which can move parallel to the line P_1M_1. It has an arrangement for rotation about a vertical axis and also for small rotation about a horizontal axis.

(iii) The plate P_2 can be rotated about a vertical axis.

(iv) The mirror M_2 has an arrangement for small rotation about a vertical axis.

(v) The plate P_1 and the mirror M_2 are both mounted on a rigid wooden beam which can be rotated about a horizontal axis parallel to the plane of P_1 or M_2. The axis of the wooden beam passes through its middle.

The above movements are sufficient to make the adjustments described below.

(*a*) The beam B can be rotated in a vertical plane because the mirror M_1 can move about a horizontal axis.

(*b*) The beam A can be rotated in a horizontal plane by turning the mirror M_2 about a vertical axis.

(*c*) The shifting of the beam B parallel to itself in a horizontal plane requires some explanation. Consider Fig. 2 (*a*). The mirror M_1 can be moved in the direction $\alpha\beta$. Suppose that $\alpha\beta\gamma\delta$ is the path of the ray when the mirror M_1 is in the position β. Let M_1 move to the position β'. The

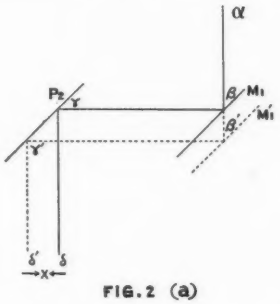

FIG. 2 (a)

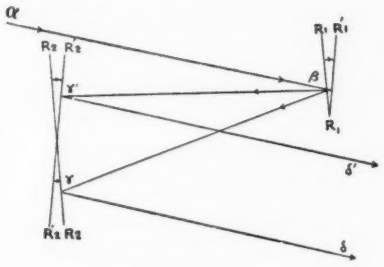

FIG. 2 (b)

path of the ray will now be $\alpha\beta'\gamma'\delta'$ with a lateral shift equal to x as indicated in the figure.

(*d*) We may now explain how the ray A can be shifted parallel to itself in the vertical plane. It may be recalled that the plate P_1 and the mirror M_2 (*vide* Fig. 1) are mounted on the same wooden beam which can be rotated about a horizontal axis parallel to the plane of M_2 or P_1. Such a rotation of the wooden beam involves a rotation of both P_1 and M_2 by exactly the same angle. The turning of P_1 deflects the ray A one way in the vertical plane but the turning of M_2 deflects the same ray in the opposite direction to

the same extent thus neutralising the rotation produced by P_1. Though these rotations neutralise each other the ray A gets a lateral shift parallel to itself in the vertical plane as shown in Fig. 2 (*b*).

Let R_1 and R_2 represent two surfaces reflecting a ray along the path $\alpha\beta\gamma\delta$. If now R_1 and R_2 rotate through the same angle and take up the positions R_1' and R_2', R_1' will now reflect the beam $\alpha\beta$ along $\beta\gamma'$ and R_2' will reflect it along $\gamma'\delta'$. The rotations are neutralised but $\gamma\delta$ is shifted parallel to itself to the position $\gamma'\delta'$.

Having described how to produce the rotations and lateral shifts of the beam A and B we proceed to show how fringes of any given (i) orientation in a vertical plane, (ii) width, and (iii) localisation may be obtained.

The light from the sodium lamp (see Fig. 1) is stopped down by a pinhole in a black screen and rendered parallel by the lens L_1. We are therefore able to see in the telescope T two images of a bright source of light situated at infinity. We now turn the mirror M_2 about a vertical axis till the two images stand one above the other. A second lens L_2 is then thrown into position at the point shown by the arrow in Fig. 1 and forms images* at O and O′ of the point source at infinity. The telescope is now focussed for the images at O and O′. The images are brought one below the other by turning the plate P_2 about a vertical axis and when they are in the same vertical straight line, they are made to coincide by turning the beam carrying P_1 and M_2 about its horizontal axis.

The lens L_2 is now removed, the telescope focussed for infinity, and once more the two images are made to stand one above the other by turning M_2 about a vertical axis. After this the lens L_2 is again thrown into position and the above operations repeated.

The optical arrangement in Fig. 1 effectually enables us to produce two cones of light emerging from P_2 which have their apexes at infinity. When the apex of one beam is made to coincide with that of the other, the position may be roughly as shown in Fig. 3 (*a*). Now when the Lens L_2 is introduced the two beams come to a focus as in Fig. 3 (*b*) at N_1 and N_2. When N_1 and N_2 are made to coincide and the lens L_2 is then removed we have the two beams as in Fig. 3 (*c*). After repeating these adjustments a number of times we are able to bring A_1 and A_2 at a desired distance apart while keeping the angle of the two beams sufficiently small and obtain bright fringes localised at O or O′ (see Fig. 1).

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* O and O′ are points which can be anywhere in the paths $P_1M_2P_2$ and $P_1M_1P_2$ respectively.

FIG. 3 (a)

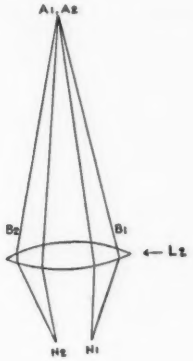

FIG. 3 (b)

FIG 3 (c)

FIG. 3 (d)

It is worth noting that while making the above adjustments with the point-sources at infinity one beam is affected, while in doing the adjustments with the localised point-sources, it is the other beam that is affected.

(i) *Orientation of fringes* :—The direction of the interference bands is at right angles to the line joining the two virtual sources of light at infinity. Therefore to adjust the direction of the fringes we have simply to change the direction of the line joining the point-sources.

(ii) *Fringe width* :—Fringe width is inversely proportional to the distance between the sources of light.

(iii) *Localisation* :—We have shown above how the fringes are localised at O or O′. If now it is desired to change the localisation, it is necessary to turn the wooden beam carrying M_2 and P_1 about its horizontal axis. This adjustment shifts the beam A vertically up or down and shifts the plane at which the two interfering beams meet, without changing the angle between them. This is made clear by Fig. 3 (*d*). Let the two beams A and B meet at O. If the beam A is shifted parallel to itself to the position A′, the point

of intersection and therefore the position of the fringes moves over to the point Q.

Lastly we may add that an improvement in the clarity of the fringes is made possible by a slight movement of M_1 parallel to the line joining P_1 and M_1.

One special advantage of this type of interferometer† is that by following the above scheme of adjustments carefully the fringes can be localised at any desired point in $P_1M_2P_2$ or $P_1M_1P_2$ (Fig. 1) without change in the width or inclination of the bands. Usually, the experimental surface or medium is inserted between M_2 and P_2 or P_1 and M_1. It is necessary to localise the fringes at the point where these objects are inserted so as to obtain the actual distortion in the fringes in their neighbourhood. When this is done the whole pattern of fringes and the object inserted can be focussed simultaneously on a screen and photographed.

Now, if we insert a horizontal hot plate into the field of the interferometer the distortion of the fringe system is seen to depend upon whether we insert it between P_1 and M_1 or M_2 and P_2 (Fig. 1).

Case (i)—

The interfering wave fronts are shown as O A (corresponding to beam A) and O B (corresponding to beam B) in Fig. 4 (*b*) where the inclination between O A and O B is shown exaggerated. Let C D indicate the position and width of the horizontal hot surface which causes the wave-front to be distorted into A E O (when inserted between M_2 and P_2 of Fig. 1) as indicated by the dotted lines above and below the surface. The whole diagram is a vertical section of the arrangement in the plane parallel to the axis of the beams and represents a side view of the wave-front. The distortion of the wave-front A O is greatest near C D, and becomes negligible some distance away from the surface. The system of fringes moves away from the surface and at the same time becomes narrow above the plate, the minimum width occurring nearest to the hot surface. Below the surface the disturbed wave front is O E and it will be seen that the fringe system will move towards the surface and widen out at the same time, the widening being maximum nearest to the surface. Fig. 4 (*a*) shows the behaviour of the interference bands above the hot surface which is inserted only half-way into the field. The position of the hot surface is indicated by an arrow.

† Localisation of fringes at any desired point in the optical system without changing the fringe width is not possible with Michelson's arrangement of the interferometer.

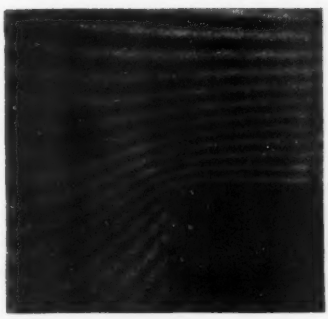

FIG. 4 (a)

FIG. 4 (c)

FIG. 4 (b)

FIG. 4 (d)

Case (ii)—

Here the wave-front affected by the hot surface inserted between P_1 and M_1 (see Fig. 1) is O B which gets distorted into O E B as in Fig. 4 (*d*). In this case the movements of the fringe system would be exactly opposite to those observed in the previous case. The fringes above the surface widen out and move towards the surface and those below it contract and move away from it. Fig. 4 (*c*) shows the behaviour of the fringes above the surface and it will be noticed that the displacement and changes in width are exactly opposite to those in Fig. 4 (*a*).

Case (i) is to be preferred for the investigations of conditions above the surface as it provides a closer system of fringes for calculating air temperatures, and case (ii) is to be preferred for studying the conditions below the hot surface. In actual working the adjustment for either (i) or (ii) can be made without changing the position of the hot plate, by merely interchanging the positions of the wave-fronts O A and O B.

3. *Method of Calculation.*

When a hot surface is introduced half way into the field of the interferometer adjusted to give horizontal fringes, the fringes get shifted. These shifts can be used for calculating the temperatures of the air layers in the neighbourhood of the hot surface. The method of calculation given below closely follows that of Kennard.‡ Consider Fig. 5 (*a*). Suppose it represents the appearance of the fringes and the hot surface when the line of sight is parallel to the axis of the interfering beams. S_1S_2 is the hot surface and F_1F_1', F_2F_2' and F_3F_3', etc., represent the fringes. Let us fix our attention on the fringe F_3F_3'. It will be noticed that the left hand and right hand extremes of the fringe are horizontal. The fringe has shifted up by an amount F_3F_3'' equal to x cm. Also let F_2F_3 be equal to y cm. Then the shift expressed in fringe-widths is equal to x/y and we know that this must be equal to the change in the optical path of the light beam perpendicular to the plane of the figure by x/y wave-lengths. We shall denote the shift x/y by Δ N (in terms of the undisturbed fringe-width).

Having shown how the shifts are measured, we proceed to derive a formula connecting Δ N with the temperature of air at the point F_3'.

If n is the refractive index and ρ the density of air we have the Lorenz-Lorentz equation :

$$\frac{n^2 - 1}{n^2 + 2} = C\rho \tag{1}$$

where C is a constant.

For air at ordinary pressures the above equation reduces to :

$$(n - 1) = \tfrac{3}{2} C\rho \tag{2}$$

If N_1 is the number of light waves in a distance equal to the width of the plate S_1S_2 normal to the plane of the paper and n_1 the refractive index of the air near it when the surface is at air temperature, and if N_2 and n_2 are the corresponding quantities when the surface S_1S_2 is hot, then

$$n_1 = \frac{N_1}{N_0}$$
$$n_2 = \frac{N_2}{N_0} \tag{3}$$

where N_0 is the number of waves over the same path in vacuum.

Further $N_0 = \dfrac{L}{\lambda_0}$, where L is the width of the plate and λ_0 the wave length *in vacuo*. From equation (2) we have :

$$n_1 - 1 = \tfrac{3}{2} C\rho_1$$

‡ *Bureau of Standards Journal of Research*, January-June 1932, **8**, 791–792.

and

$$n_2 - 1 = \tfrac{3}{2} C\rho_2 \tag{4}$$

corresponding to the room temperature T_1 and the higher temperature T_2 at some point near the hot surface (T_1 and T_2 are in degrees absolute).

From (4) by subtraction :

$$n_1 - n_2 = \tfrac{3}{2} (\rho_1 - \rho_2) C \tag{5}$$

$$N_1 - N_1 = \tfrac{3}{2} C\rho_1 \frac{I}{\lambda_0}\left(1 - \frac{\rho_2}{\rho_1}\right) = (n_1 - 1)\frac{I}{\lambda_0}\left(1 - \frac{\rho_2}{\rho_1}\right) \tag{6}$$

Assuming that the pressure remains sensibly constant we have :

$$\frac{\rho_2}{\rho_1} = \frac{T_1}{T_2} \tag{7}$$

so that

$$\Delta N = (n_1 - 1)\frac{I}{\lambda_0} \cdot \frac{T_2 - T_1}{T_2} \tag{8}$$

where ΔN is put for $N_1 - N_2$. Equation (8) may be expressed as :

$$T_2 - T_1 = T_1 \frac{\Delta N}{\frac{n_1 - 1}{\lambda_0} L - \Delta N}$$

This relation can now be used for calculating T_2 at various distances away from the hot surface when T_1 the absolute temperature of room, I, the width of the surface, n_1 the refractive index§ under room conditions and ΔN the shift in fringe-widths are known.

4. Method of End-Correction.

An interference fringe which is horizontal in the undisturbed portion of the field becomes horizontal above the hot plate only after passing through a certain region near the edge where it is inclined. From the variation of the slope of the fringe with distance it is possible to compute the end correction at the edge of the plate which is in the direction of the axis of the interferometer and apply this correction to the two edges of the plate which the beam of the light has to pass before it interferes with the other beam.

This method of applying the end correction is independent of the usual assumption with regard to equality of air temperature and the plate temperature at the hot surface.

Suppose we are looking at a horizontal hot surface from above. Let then S_1, S_2, S_3, S_4 represent the hot surface [see Fig. 5 (*b*)]. Now it is not only the air above the path S_4S_1 which will be hot but also the air at U and U′ near the edges of the plate. It is this that necessitates an end correction.

§ T_1 is actually measured and n_1 is calculated from the value of n_0 at N. T. P. for the actual value of humidity, pressure and temperature in the room during each experiment.

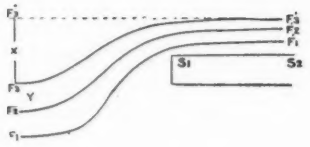

FIG. 5 (a)

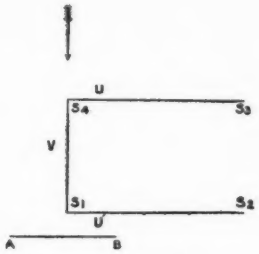

FIG. 5 (b)

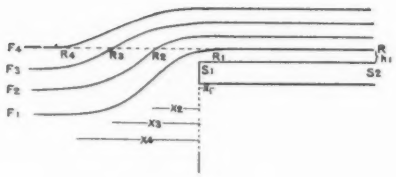

FIG. 5 (c)

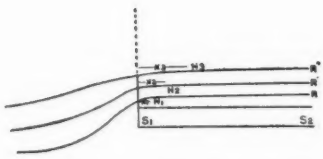

FIG. 5 (d)

Let the arrow represent the direction of the interfering beam of light and let AB represent the width of the field of view of the interferometer. Use is now made of the fact that the air at V is affected similarly to that at U and U′. Since the hot surface is only partly inserted in the field of view the fringe shifts in the left-hand part of the field of view must be attributed to the end effects alone.

Now consider Fig. 5 (*c*) which represents a vertical section of the hot plate half inserted into the interference field. S_1S_2 represents the hot plate. The bent lines are the interference bands.

Let it now be required to find the end correction at R which is h_1 cm. above the hot surface. Consider the points R_1, R_2, R_3, etc. on a line (dotted in the figure) drawn through R parallel to the hot surface. At R_2 the fringe shift is two fringe-widths. This shift must be attributed to a horizontal column of hot air at the level of R having its axis at a distance of x_2 cms. from the edge S_1 of the hot surface, and along the line of sight. The length of this column was assumed to a first approximation to be equal to L_0 the width of the hot surface. Therefore at a distance x_2 cm. the shift is $2/L_0$ fringe-widths per cm.

A number of values of the distance beyond the hot plate and the fringe shifts per cm. at these points are actually measured. From these a curve showing

the relation between the fringe shift per cm. and the distance x away from the edge is plotted. Let us now suppose that at a distance x from the edge of the plate the fringe shift per cm. is $F(x)$. The total fringe shift is then given by $\int F(x)dx$ the limits of integration being $x = 0$ and $x = X$ where X is the distance of a point towards the undisturbed portion of the field where the fringe shift vanishes.

The value of the integral as obtained from the graph referred to above therefore gives the magnitude of the shifts due to the end effects at the edges U and U′ Fig. 5 (*b*), and must therefore be subtracted from the observed shift at R. It is thus possible to find from separate graphs of $F(x)$ against x the end correction for different distances h_2, h_3, etc. above the hot surface. From Fig. 5 (*d*) it may be seen that the point where the interference band stops bending and becomes straight creeps in towards the plate as we proceed away from the surface (*vide* points N_1, N_2, N_3, etc.). This means that the end error begins to the left of N_1, N_2, N_3, etc. and that therefore it is only to the right of these points that the refractive index is constant. For the fringe R′ for example, we must take only $(L_0 - 2X_2)$ as the constant refractive index path (where x_2 represents the distance of N_2 from the edge).

5. *Temperature Distribution between a Horizontal Hot Surface Above and a Horizontal Cold Surface Below.*

We have already seen in our smoke experiments (see Part I) that when the separation between the two surfaces is of the order of 2 mm. or less the space between the surface is *totally* devoid of convection and that any smoke let into the air cell is rapidly repelled and deposited on the cold surface. There is no doubt that separations of the order of 2 mm. are to be preferred for the measurement of the heat conductivity in gases. In the experiments of Hercus and Laby[3] the separation used was as much as 6·28 mm. (temperature difference between the hot and cold surfaces was about 20° C.) and it was not therefore justifiable to assume that convection currents would have been absent at a pressure of one atmosphere. A reference to Figs. 2 and 3 of Plate XI in the earlier paper‖ will show that when the separation is 6·28 mm. the nature of the convection in the air cell would be intermediate between those seen in Figs. 2 and 3. Another point to note is that so long as traces of convection are present in the air gap it may not be justifiable to assume a constant temperature gradient from the hot surface to the cold one.

In the present section we shall discuss the interferometric measurements of temperature when the thickness of the air cell was 1·61 mm. and 0·77 mm.

‖ Paranjpe, *Proc. Ind. Acad. Sci.*, 1936, **4**, 423.

respectively. In Plate XV, Figs. (*a*) and (*b*), the appearances of the interference fringes are shown enlarged for these two cases. The left half of each picture shows the air gap between the hot surface above and the cold surface below both of which are 5·2 cm. in width; the right half shows the undisturbed portion of the interference field. The temperatures of the two surfaces were maintained at about 83° C. and 33° C. respectively or with a temperature difference of the order of 50° C. The upper surface was heated electrically and the cold surface was maintained at a constant temperature by circulating water. The temperatures of the two surfaces were measured by means of thermal junctions in the usual way.

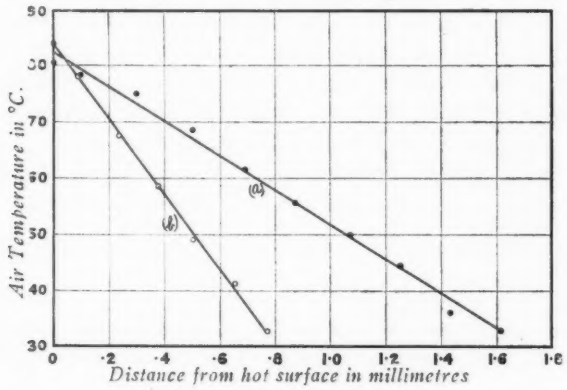

FIG. 6.

The variation of temperature with distance between the two surfaces was calculated by employing the methods described in the two preceding sections. The temperature-distance relations are as shown by the curves (*a*) and (*b*) in Fig. 6.

It is interesting to note that the distribution of temperature is sensibly linear in both the cases.

6. *Summary.*

The paper describes an interferometric method of measuring the temperature distribution near hot surfaces. The details of the method and the various precautions to be taken are discussed. The distribution of temperature in the case of a horizontal air cell between a hot surface above and a cold surface below is discussed in relation to convection and the importance of using small air gaps (2 mm. or less) in thermal conductivity measurements is pointed out. Pictures of the interference pattern when the air cell is 1·61 mm.

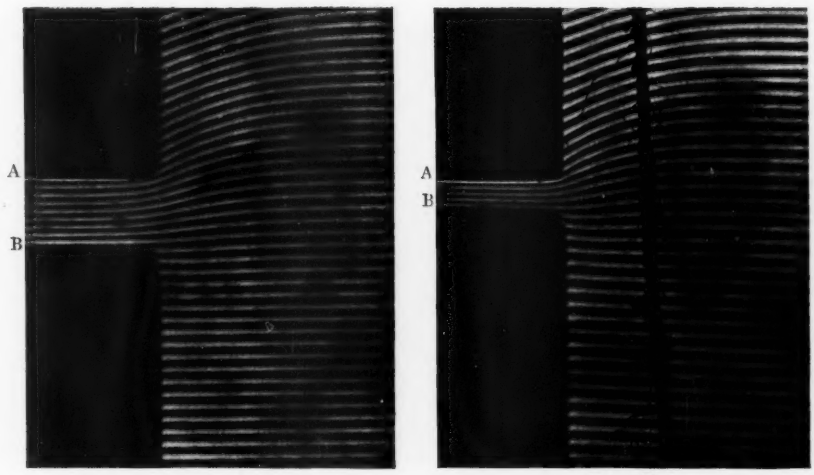

FIG. (*a*) FIG. (*b*)

A is the upper hot surface and B the cold surface below it. AB = 1·61 mm. in fig. (*a*) and 0·77 mm. in fig. (*b*). (The rugged object stretching across the field of view in fig. (*b*) is a piece of thread suspended in the plane in which the fringes are localized; it was accidentally not removed before the picture was exposed, but shows the accuracy with which localization can be achieved.)

and 0·77 mm. thick are given along with the temperature distributions calculated from these pictures.

In conclusion, the author's best thanks are due to Dr. L. A. Ramdas for the suggestion of the problem and guidance in the course of the investigation. He is also grateful to the Director-General of Observatories for the facilities given at the laboratories of the Meteorological Office at Poona and to Professor S. D. Bhave, S. P. College, Poona, for the loan of the interferometer.

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1. Paranjpe, M. K., *Proc. Ind. Acad. Sci.*, 1936, **4**, 423.
2. Ramdas, L. A., and Paranjpe, M. K., *Current Science*, March 1936, 642.
3. Hercus and Laby, *Proc. Roy. Soc.*, 1919, **95**, 190.

ON A RELATION BETWEEN TWO CONJECTURES OF THE THEORY OF NUMBERS.

By S. Chowla.

(*Government College, Lahore.*)

Received November 11, 1936.

§1. Let $r_{k,s}(n)$ denote the number of representations of n as a sum of s kth powers of integers ≥ 0. Since $r_{k,2}(n) = O(n^{\epsilon})$ for every positive ϵ, we have

$$r_{k,k}(n) = O\left(n^{1-\frac{2}{k}+\epsilon}\right)$$

and no better result is known. Denote by (A_s) the unproved result that

$$(A_s) \qquad r_{k,k}(n) = O\left(n^{\frac{s}{k}}\right)$$

where $k \geqslant 5$ and s is a positive integer $\leq k-3$. Denote by (B_s) the conjecture that

(B_s) $\sum_{m=1}^{k-s} x_m^k = \sum_{m=1}^{k-s} y_m^k$ *has a non-trivial solution in positive integers* $x_1, x_2,$ *etc.*, $y_1, y_2,$ *etc.*

Then we have the

*Theorem.** *If* (A_s) *is false then* (B_s) *is true, and conversely.*

In other words at least one of (two desirable results) (A_s) and (B_s) is true.

Proof. If (B_s) is false, then

$$r_{k,k-s}(n) = O(1)$$

whence

$$r_{k,k-s+1}(n) = O\left(n^{\frac{1}{k}}\right)$$

$$r_{k,k-s+2}(n) = O\left(n^{\frac{2}{k}}\right)$$

etc.

$$r_{k,k}(n) = O\left(n^{\frac{s}{k}}\right)$$

* The proof shows that the result is trivial; my object is to draw attention to the conjectures themselves.

i.e., if (B_s) *is false then* (A_s) *is true.* Conversely, if (A_s) is false, it follows that (B_s) must be true.

§2. Note the special case when $s = 3$ $(k \geqslant 6)$. at least one of the following conjectures is true :

$$\text{(A)} \qquad a_1^k + a_2^k + a_3^k = b_1^k + b_2^k + b_3^k$$

has a non-trivial solution in positive integers, a_1, a_2, a_3, b_1, b_2, b_3.

$$\text{(B)} \qquad r_{k,k}(n) = O\left(n^{\frac{k-3}{k}}\right)$$

It seems to the writer that (A) is *not likely* to be proved in the near future. On the other hand, it is possible that (B), which asserts so much less than " Hypothesis K " of Hardy and Littlewood, is not a difficult result. We observe also that (A) *may be false, for solutions of* (A) are not known even for $k = 5$.

THE NUMBER OF SOLUTIONS OF A CONGRUENCE IN TWO VARIABLES.

By Inder Chowla,
Research Scholar, Panjab University.

Received December 11, 1936.
(Communicated by Dr. S. Chowla.)

1. The object of this paper is to prove *by an entirely new method*, the following well-known theorem discussed partially by Dickson and Hurwitz and more completely by Mordell (*Math. Ztschr.*, 1933).

Theorem. The number N, *of solutions of*

$$x^k + y^k \equiv n (p^\theta) \tag{1}$$

where $(n, p) = 1$, *satisfies*

$$| \mathrm{N} - p^\theta | \leqslant (k-1)^2 \, p^{\theta - \frac{1}{2}}$$

Hence, in particular, (1) *always has a solution if* $\mathrm{p} > (\mathrm{k}-1)^4$.

2. *Proof.* Write

$$\mathrm{S}_\rho = \sum_{h=0}^{q-1} \rho^{h^k}$$

where ρ is a primitive qth root of 1.

$$\mathrm{A}(q) = \sum_{\rho} \left(\frac{\mathrm{S}_\rho}{q} \right)^s \rho^{-n}$$

where ρ runs over the $\phi(q)$ primitive qth roots of 1.

$$\chi_p = 1 + \mathrm{A}(p) + \mathrm{A}(p^2) + \cdots$$

$\mathrm{M}(p^l, n)$ is the number of solutions of

$$h_1^k + \cdots + h_s^k \equiv n (p^l)$$
$$\text{with } 0 \leqslant h_r < p^l \; (1 \leqslant r \leqslant s).$$

We need the following lemmas

Lemma 1. $1 + \mathrm{A}(p) + \mathrm{A}(p^2) + \cdots + \mathrm{A}(p^l) = p^{-(s-1)l} \, \mathrm{M}(p^l, n)$.

Lemma 2. $|\mathrm{A}(p)| \leqslant (k-1)^s \, p^{\frac{1}{2} - s/2}$, if $p \nmid n$.

Lemma 3. If $p \nmid 2kn$, then $\mathrm{A}(p^l) = 0$ for $l > 1$ and hence $\chi_p = 1 + \mathrm{A}(p)$.

[See Landau, *Zahlentheorie*, Bd. 1, theorems 286, 317, 293 (Vorbemerkungen).]

3. In the above lemmas we take $s = 2$. Then if $p \nmid 2kn$, we get (lemmas 1 and 3).

$$\chi_p = 1 + \mathrm{A}(p) = \sum_{\lambda=0}^{l} \mathrm{A}(p^\lambda)$$
$$= p^{-l}\,\mathrm{M}(p^l, n).$$

From this and lemma 2 we get

$$|\mathrm{M}(p^l, n) - p^l| \leqslant (k-1)^2\, p^{l-\frac{1}{2}}.$$

This is our result with l for θ.

THE STRUCTURE OF THIN METALLIC FILMS.

By S. Rama Swamy.

(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

Received December 3, 1936.

1. Introduction.

In an earlier paper,[1] the scattering of light by thin films of metal obtained by evaporation *in vacuo*, has been studied. Some interesting results obtained were given and it was found that a metallic film prepared by the method given in that paper could be divided into three parts, *viz.*, a central metallic part which was highly conducting and scattered very little light, a part which scattered light intensely and had a high electrical resistance, and a part which also scattered light though a little more feebly but was non-conducting. It was suggested from these results that the metallic film has three possible different states: a crystalline state where there is complete regularity of arrangement of atoms and consequently very little scattering of light, a two dimensional gaseous state with random distribution, and an intermediate state between these two. This means that in a metallic film it is possible to have an amorphous modification of the metal. Kramer[2] and Zahn and Kramer[3] have been able to obtain non-conducting films of iron, nickel, platinum, zinc, tin, etc., by cathodic sputtering as also by evaporation *in vacuo*. They suggest that in the anomalous non-conducting condition the metallic film is amorphous. They also find that on heating above a certain critical temperature the non-conducting modification becomes highly conducting. They suggest that this is due to the formation of a metallic lattice at the critical temperature.

All evidence obtained so far regarding the amorphous state of thin metallic films is, however, indirect. More direct evidence can be obtained by examining them by the method of electron diffraction which has been developed in recent years by G. P. Thomson,[4] G. I. Finch[5] and others. The surface of polished metal, for instance, has been shown to be amorphous by

[1] S. Rama Swamy, *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 347-353.
[2] J. Kramer, *Ann. der Physik*, 1934, **19**, 37-64.
[3] H. Zahn and J. Kramer, *Zs. Phys.*, 1933, **86**, 413-420.
[4] G. P. Thomson and G. G. Fraser, *Proc. Roy. Soc.*, A, 1930, **128**, 641.
[5] G. I. Finch, A. G. Quarrel and H. Wilman, *Trans. Farad. Soc.*, 1935, **31**, 1051.

this method.[6,7,8] The present work was taken up with a view to obtain direct evidence of the amorphous state of metals in thin films by their study with the help of the method of electron diffraction.

2. Experimental.

Films of silver and gold were obtained by evaporation of the metals in vacuo in a slightly modified form of the apparatus previously employed.[9] The modification consisted firstly of an improved method of passing the heating leads through the bed-plate as shown in Fig. 1. The heating lead *C* (Fig. 1) which was a stout copper wire passed through a small brass plate *B* to which it was soldered to make a vacuum tight joint. The plate *B* was then stuck on with Metropolitan Vickers' black wax, to one of the faces of a piece of plate glass *A*, both sides of which had been ground flat with very fine carborundum powder. A glass tube *E*, the ends of which were ground flat was slipped over *C*, as shown, for purposes of insulation. The whole arrangement was then passed through holes in the bed-plate *D* as shown, with a thread of Metropolitan Vickers' vacuum putty *F* between the ground-glass piece and the bed-plate and pressed home. The vacuum further pulled this down tight thus forming a very effective joint. Further, instead of the conically wound heating spiral previously used, the type of filament recommended by Ritschl[10] was used. The metals were evaporated on to surfaces of freshly split pieces of mica kept inclined in the apparatus as previously.

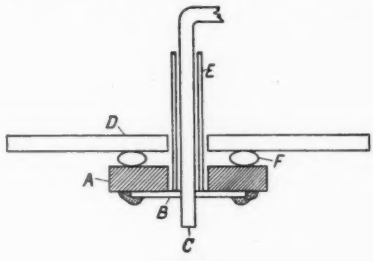

FIG. 1.

The electron diffraction camera was a standard outfit made by "Seemann Laboratorium" using a hot filament of tungsten as the electron emitter. The high potential necessary for working the apparatus was supplied by a standard equipment consisting of a high tension transformer, two hot

[6] R. C. French, *Proc. Roy. Soc.*, A, 1930, **140**, 637.
[7] C. S. Lees, *Trans. Farad. Soc.*, 1935, **31**, 1102.
[8] H. G. Hopkins, *Trans. Ferad. Soc.*, 1935, **31**, 1095.
[9] S. Rama Swamy, *loc. cit.*
[10] R. Ritschl, *Zs. Physik*, 1931, **69**, 578.

cathode rectifiers and two suitable condensers connected in the Greinacher circuit. The outfit was fed on the primary side by a suitable motor generator set working off the 25 cycle 220 volt A.C. supply of the Institute. The potential applied to the electron diffraction tube by these means was found to be quite steady and could be maintained so over quarter of an hour after thoroughly degassing the hot cathode.

The specimens used for examination were cut from various parts of the mica on which the metallic film had been deposited. They were about 2 mm. wide and about a centimetre or so long. In order to avoid burring of the edges of the specimens, which would either hide the diffraction pattern produced by the metallic film or give a pattern of mica dust, the following procedure was adopted. The specimen was kept on a piece of clean Bristol board with the metallic film side up and the edges cut by a single stroke of a keen edged razor held slightly inclined.

Previously to introducing them in the diffraction camera the specimens were soaked and washed in petroleum ether about half a dozen times in order to remove all traces of grease which may have been present. Immediately after washing, they were inserted in the electron diffraction camera and the pattern given by the metallic film on the specimen strip obtained by the well-known method of reflection of G. P. Thomson. Some of the patterns obtained are reproduced in Figs. 2–5.

3. Results.

In Fig. 2 is given a pattern obtained from the central opaque portion of a gold film. This part of the film does not scatter any light whatever. From the pattern in Fig. 2 we find that this part of the film consists of preferentially oriented crystals, the preferred plane being *111* which was parallel to the surface of deposition.

The next part of the gold film studied was green by transmitted light and had the characteristic golden colour by reflected light. The pattern obtained from this part is shown in Fig. 3 and consists of continuous rings showing random orientation of the crystals in the film.

Fig. 4 is a pattern obtained from a part just prior to the start of the intense scattering of light. The pattern consists of rings as before but they are definitely diffuse and the innermost rings (*111* and *200*) are beginning to fuse together showing that the crystallites are much smaller than in the previous part.

In Fig. 5 is given the pattern produced by the part of the film just at the start of the intense scattering of light. In the case of gold films the colour

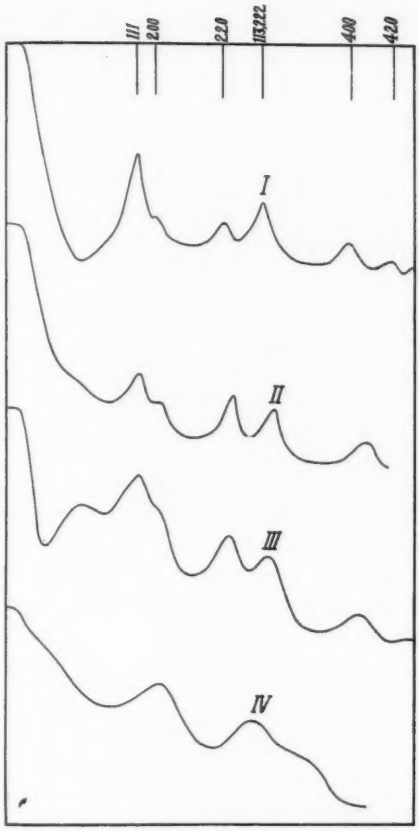

FIG. 6.

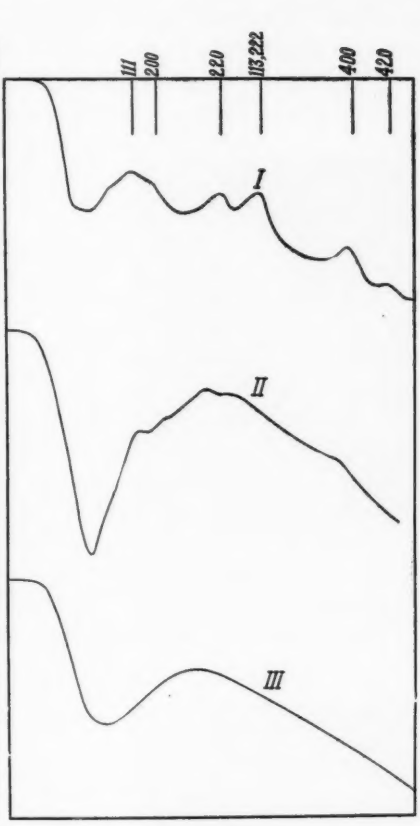

FIG. 7.

of this portion by scattered light is a deep red while for silver it is orange. The pattern from this part of the film consists of one or two haloes, as shown in Fig. 5, indicating thereby that the film is no longer crystalline but amorphous.

It was not possible even to observe the pattern given by the next non-conducting part of the film due to its rapid charging up by the electron beam. But from a study of the previous pattern and the manner in which the sharp rings gradually become diffuse haloes one may reasonably infer that this part of the film is amorphous.

Microphotometer records of these patterns are given in Fig. 6 which bring out the points mentioned above in a striking manner. In Fig. 6, *I* and *II* correspond to the opaque and transparent metallic portions of the

gold film ; *III* corresponds to the part just before the scattering of light starts and *IV* to the portion immediately after the start of the scattering.

Exactly similar results were obtained with silver films, microphotometer records of the patterns given by one of them being reproduced in Fig. 7. Here *I* corresponds to the central metallic part of the film, *II* to the part just before the scattering of light starts and *III* to the part which scatters light.

It is with much pleasure that I take this opportunity to express my sincere thanks to Sir C. V. Raman, F.R.S., for the kind and helpful interest he has taken in the progress of this work and for the facilities afforded in his laboratory for its execution.

4. Summary.

The structure of thin films of gold and silver obtained by evaporation *in vacuo* has been studied by electron diffraction methods. Direct evidence has been obtained for the existence of these metals in the amorphous state as suggested in an earlier paper by the author. Films of gold and silver which are thin enough to scatter light, as discussed in the earlier paper, are found to give electron diffraction patterns corresponding to an amorphous structure. Thicker films having metallic reflection and high electrical conductivity give patterns corresponding to a polycrystalline structure.

FIG. 2.

FIG. 4.

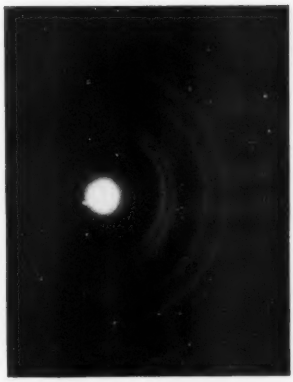

FIG. 3.

FIG. 5.

Electro diffraction patterns of Gold film on mica.

X-RAY DIFFRACTION AND ELECTROLYTIC DISSOCIATION—I.

Sulphuric Acid and Sulphates.

By R. S. Krishnan.
(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

Received December 11, 1936.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

It is well known that a study of the Raman effect offers a means of determining the degree and the nature of dissociation of concentrated solutions and thus supplies valuable information with respect to the physical and chemical properties of such solutions. Studies of Raman effect in concentrated solutions indicate that normal salts are completely dissociated at all concentrations and that in strong acids and its acid salts the degree of dissociation increases with dilution. It is however of interest to consider whether any information could be gained from a study of X-ray diffraction in such solutions, when the concentration of the solution is changed. In the present investigation, therefore, the diffraction of X-rays by aqueous solutions of sulphuric acid, its normal and acid salts has been studied in detail. An attempt has been made to correlate the results with those obtained from Raman effect data.

H. Shiba and T. Walanabe[1] were the first to study the diffraction of X-rays by aqueous solutions of sulphuric acid at four different concentrations. They reported only a contraction of the halo with increase in concentration. In their experiments the central undeflected beam of X-rays was not cut off and consequently they were not able to record any other change in the diffraction pattern with change in concentration. J. A. Prins[2] has studied the X-ray diffraction in solutions of heavy ions in water in order to get an idea about the distribution of ions in solutions. He finds that there are three types of solutions. The diffraction patterns of saturated solutions of

[1] H. Shiba and T. Walanabe, *Scientific Papers of the Institute of Physical and Chemical Research*, 1929, **10**, 187.

[2] J. A. Prins, *Physica*, 1934, **1**, 1171.
J. A. Prins and R. Fonteyene, *Physica*, 1935, **2**, 570 & 1016.
J. A. Prins, *Jour. Chem. Phys.*, 1935, **3**, 72.

the first type of salts consist mainly of a pronounced ring, shifting to smaller angles and getting fainter with increasing dilution. This indicates a more or less regular arrangement (which he calls as *super-arrangement*) of ions. Another kind of pattern is exhibited by solutions of the second type. In this case, the intensity does not show pronounced maxima and minima. Moreover it does not decrease markedly when the diffraction angle tends to zero. Prins tries to explain this behaviour by assuming the existence of a large fraction of undissociated molecules, with a gaseous distribution. The third type of solutions yields a broad ring the position of which is independent of concentration. This fact is explained by ascribing this ring mainly to the interference between the scattering from a heavy ion and that from water molecules around it.

Experimental Technique.

The arrangement of apparatus in the present investigation was the same as in the powder photograph method of Debye and Scherrer. A metal Shearer tube with molybdenum anti-cathode was used as the source of X-rays. The tube was excited by a transformer, the voltage applied being in the neighbourhood of 50 K.V. The current in the X-ray tube was maintained at about 7 milliamperes. A cylindrical block of lead (5 cm. long and 3 cm. in diameter) containing a fine hole (0·8 mm. in diameter for the first 3 cm. length of the block and 1·6 mm. in diameter for the remaining 2 cm. length) drilled through its centre was used as the slit for the X-ray beam. Thin-walled glass cells were employed as the container for the liquid studied. The photographic plate was kept at a distance of 6·5 cm. from the cell containing the liquid. A thick lead disc of sufficient diameter was fixed in front of the photographic plate to cut off the central undeflected beam of X-rays. A trial photograph was taken with the container alone. The container did not give any appreciable diffraction pattern even after a prolonged exposure. X-ray diffraction photographs were taken with the following solutions: (*a*) sulphuric acid at the following concentrations 100%, 95%, 80%, 50%, 30%, and 10%, (*b*) water, (*c*) 34% and 10% solutions of potassium bisulphate, (*d*) 20% solution of potassium sulphate and (*e*) 20% solution of lithium sulphate. The sulphuric acid used was Kahlbaum's analytical reagent. The time of exposure in every case was 6 hours.

Results.

The results obtained are tabulated below. Measurements were made from the negatives visually. Column 2 in the table gives the scattering angle for the direction of maximum intensity in the halo. Column 3 represents the corresponding spacing calculated from the Bragg formula

$a = \frac{\lambda}{2 \sin \theta/2}$ as suggested by Raman and Ramanathan.[3] Columns 4 and 5 give the spacings calculated similarly, corresponding to the inner and outer limits to which the halo extends. In column 6 is given the value of $\sqrt[3]{\frac{m}{d}}$ where m = the actual weight of one molecule of the substance and d is the density in bulk. The photographs are reproduced in Plates XVII and XVIII.

For 100% sulphuric acid only one sharp intense ring is obtained with very little scattering on either side of the principal halo. The addition of a small quantity of water to the pure acid results in a widening of the ring for

TABLE I.

Mo. anti-cathode. ($\lambda = 0{\cdot}710$ A.U.)

Liquid	θ	$a = \frac{\lambda}{2 \sin \theta/2}$ A.U.	Spacing inner limit A.U.	Spacing outer limit A.U.	$\sqrt[3]{\frac{m}{d}}$ A.U.
Sulphuric acid (100%)	9° 36′	4·24	4·9	3·77	4·45
,, (95%)	9° 49′	4·15	5·16	3·36	..
,, (80%)	9° 49′	4·15	5·8	3·13	..
,, (50%)	..	..	..	2·95	..
,, (30%)	12° 9′	3·36	3·77	2·95	..
,, (10%)	12° 35′	3·29	3·77	2·87	..
Water	12° 35′	3·29	3·60	2·95	3·1
$KHSO_4$ solution (34%)	12° 9′	3·36	3·77	2·95	..
,, (10%)	13°	3·13	3·77	2·7	..
K_2SO_4 solution (20%)	13°	3·13	3·77	2·7	..
Li_2SO_4 solution (20%)	13°	3·13	3·6	2·79	..

the latter and makes its edges very diffuse. At the same time the maximum slowly shifts to larger angles. With further dilution the scattering at small

[3] C. V. Raman and K. R. Ramanathan, *Proc. Ind. Assoc. F. Culti. Sci.*, 1923, **8**, 127.

angles becomes prominent. At about 50% concentration no definite ring is obtained but only a corona surrounding the central spot, the diameter of the edge of the corona corresponding to the diameter of the water ring. With further dilutions the halo again appears, the maximum of which shifts to larger and larger angles, and finally coincides with that of water in very dilute solutions. The scattering at small angles is maximum for a 50% solution and as the concentration falls off it becomes less and less intense. Dilute solutions give in addition to the ring for water, a diffraction corona immediately surrounding the direction of the primary beam. This corona may be ascribed to the scattering of X-rays by the ions of the solute distributed at random. Almost identical diffraction patterns are obtained with 30% sulphuric acid solution and 34% potassium bisulphate solution. The diameter and width of the principal halo are the same for 10% H_2SO_4, 10% $KHSO_4$, 20% K_2SO_4 and 20% Li_2SO_4 solution.

Discussion of the Results.

The presence of a well defined ring with very little general scattering at small and large angles in the diffraction pattern of the pure acid (100%) is indicative of the existence of orderly arrangement of molecules. The interpretation of this single maximum is not very difficult, for the molecule of this acid possesses more or less a symmetrical tetrahedral structure and we should therefore expect only one maximum corresponding to the average dimension of the molecule. Associated liquids, in general, exhibit in addition to the principal maximum a secondary maximum or a corona surrounding the centre depending upon the extent of association. It is rather surprising to note that sulphuric acid, although it is highly associated, does not give rise to a secondary maximum or a corona. From other considerations it has been shown that the number of molecules in every associated group is about forty. The regularity of arrangement of molecules in the individual groups and the absence of free single molecules may be responsible for the production of such a simple diffraction pattern.

In order to understand the effect of dilution on the diffraction pattern, it is necessary to know something about the nature of ionisation as revealed by Raman effect studies. Raman spectra of sulphuric acid and its solutions have been studied in detail by Woodward and Horner,[4] Bell and Jeppesen[5] and very recently by Venkateswaran.[6] They have clearly shown that the dissociation of sulphuric acid in water takes place in stages.

[4] L. A. Woodward and R. G. Horner, *Proc. Roy. Soc.*, 1934, **144**, 129.
[5] Bell and Jeppesen, *Journ. Chem. Phys.*, 1935, **3**, 245.
[6] C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 174.

$$H_2SO_4 \rightarrow \overset{+}{H} + H\overline{SO}_4 ; \quad H\overline{SO}_4 \rightarrow \overset{+}{H} + \overline{SO}_4$$

$H\overline{SO}_4$ ion is completely absent in the 100% acid. The first stage of ionisation begins with the addition of a small quantity of water. At about 50% concentration the $\overline{SO}_4$ ion makes its appearance. At lower concentrations it predominates. The H_2SO_4 molecules decrease rapidly in number as the dilution progresses. W. H. Shaffer and D. M. Cameron[7] have shown that the ionisation of $KHSO_4$ also takes place in two stages as indicated below :—

$$KHSO_4 \rightarrow \overset{+}{K} + H\overline{SO}_4 ; \quad H\overline{SO}_4 \rightarrow \overset{+}{H} + \overline{SO}_4$$

The first stage of ionisation produces only a broadening of the principal halo of the diffraction pattern and makes its edges more and more diffuse. This is because the first stage of ionisation produces only $H\overline{SO}_4$ ions which are almost of the same size and structure as the H_2SO_4 molecule. The general scattering begins to appear due to the presence of some ions distributed at random. The 50% solution contains some unionised molecules, $H\overline{SO}_4$ ions, $\overline{SO}_4$ ions, $\overset{+}{H}$ ions and water molecules. As there is no predominance of one particular set of ions, the distribution of all these ions will be more or less chaotic with the result that only a general scattering is produced by the molecules and the ions, the intensity concentrating round the centre in the case of heavy ions or spreading throughout a larger area in the case of light ions. This type of diffraction pattern corresponds to that obtained by Prins[8] in the case of the second type of solutions. At further dilutions the ring makes its appearance again. As water forms the predominant component at these dilutions the diameter of the ring approximates to that of pure water ring. The 30% solution does not contain any undissociated molecule but only $\overline{SO}_4$ and $H\overline{SO}_4$ ions, its diffraction pattern should therefore be similar to that of 34% $KHSO_4$ solution in which also these ions are present. The normal salts are completely dissociated. Dilute solutions of H_2SO_4 and $KHSO_4$ are also completely ionised. This explains why the general form of the diffraction pattern and the distribution of intensity remain the same in the following four solutions, namely, 10% H_2SO_4, 10% $KHSO_4$, 20% K_2SO_4 and 20% Li_2SO_4. But the general scattering is much more intense in the case 10% $KHSO_4$ and 20% K_2SO_4 than in the other two cases, probably due to the presence of heavy potassium ions.

In conclusion, the author takes this opportunity to thank Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his helpful interest in the work.

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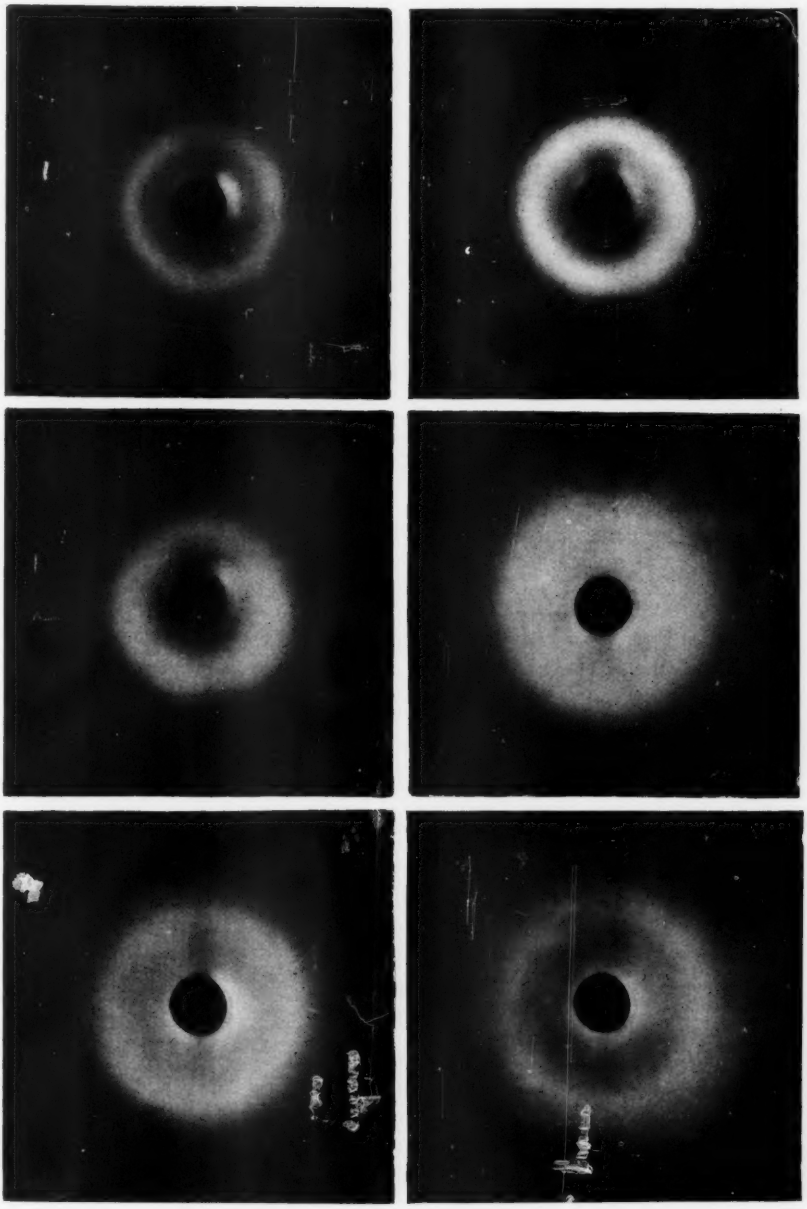
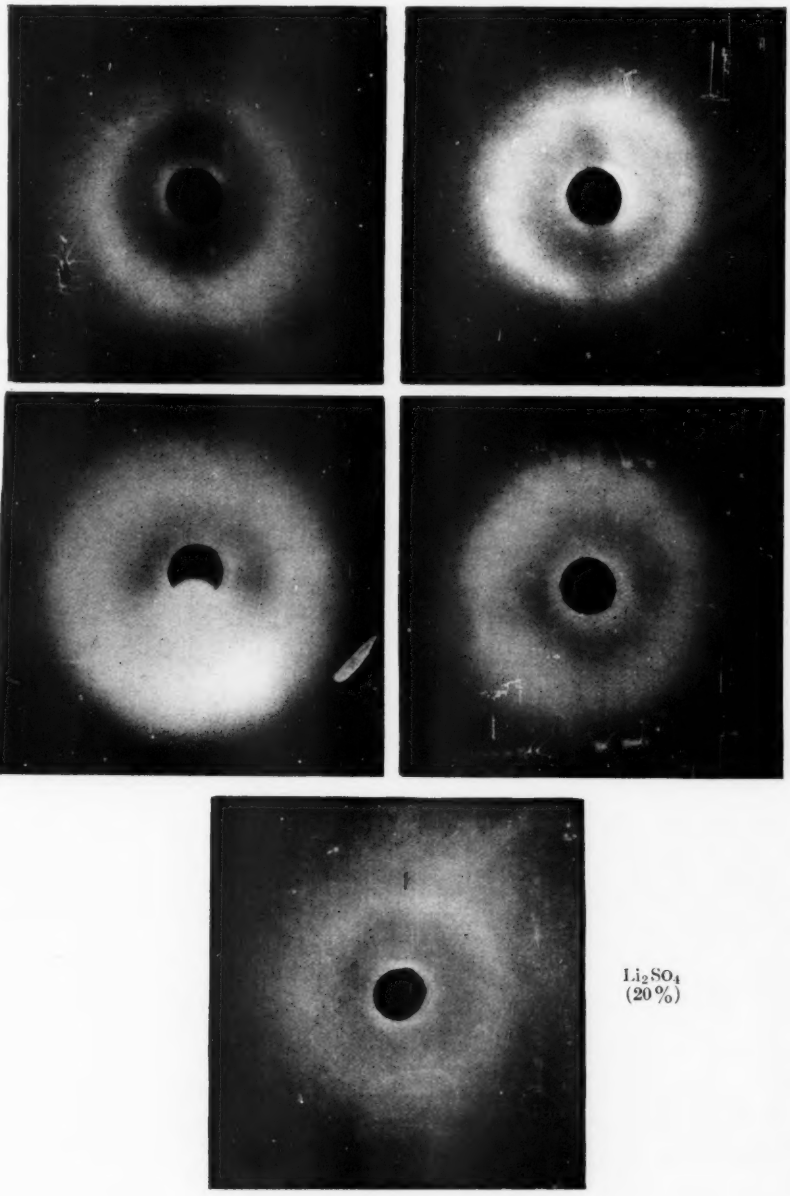
[7] W. H. Shaffer and D. M. Cameron, *Journ. Chem. Phys.*, 1936, **4**, 392.
[8] J. A. Prins, *loc. cit.*

Summary.

X-ray diffraction of the aqueous solutions of sulphuric acid, bisulphates and sulphates has been studied. 100% sulphuric acid gives only one sharp intense maximum with very little scattering on either side. On dilution with water the ring becomes broader and more diffuse. 50% solution of the acid gives only a bright corona surrounding the central spot, the diameter of the edge of the corona corresponding to that of the water ring. With further dilutions the halo again appears, the maximum of which coincides with that of water in very dilute solutions. 34% $KHSO_4$ and 30% H_2SO_4 give identical diffraction patterns. Dilute solutions of H_2SO_4 and $KHSO_4$ and solutions of the sulphates also give similar patterns. It has been pointed out that step-wise dissociation of sulphuric acid and bisulphates is responsible for the observed diffraction patterns. An attempt has been made to correlate the results obtained by X-ray diffraction experiment with those obtained from Raman effect studies of such solutions by the previous investigators.


H_2SO_4 (100%)
H_2SO_4 (95%)
H_2SO_4 (80%)
H_2SO_4 (50%)
H_2SO_4 (30%)
H_2SO_4 (10%)


Water
KHSO4 (34%)
K2SO4 (20 %)
KHSO4 (10%)
Li2SO4 (20%)

LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part IV. Elasticity Constants of Calcite.

By B. Y. Oke.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received December 11, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

The three previous papers,[1] under the same title, will be quoted herein as I, II and III respectively. In this part we proceed with the calculation of such elasticity constants of calcite, as do not essentially depend on ionic deformations. The method is exactly the same as used in II for the calculation of the elasticity constants of aragonite. Thus c_{ij} consists of two parts c_{ij}^e and c_{ij}^r due, respectively, to the electro-static and the repulsive forces. These two parts will be calculated separately.

§1. *Systems of Parallel Neutral Planes.*

Fig. 1 gives the projection of the crystal on x–y plane and Fig. 2 on the

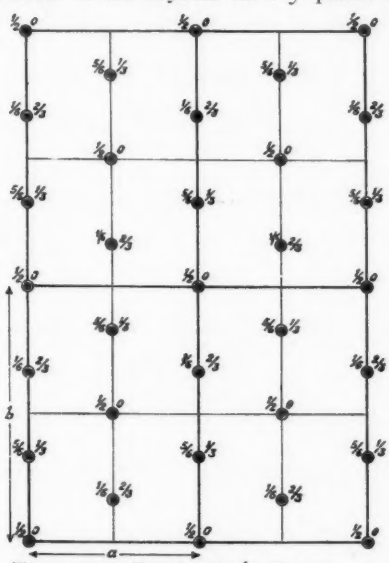


Fig. 1.

[1] B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, **4**, 1, 514 and 525.

y–z plane. The numbers in the figures denote the "heights" as multiples c and a [III (1, 1)], above the planes $z = 0$ and $x = 0$ respectively.

We take the following three systems of parallel neutral planes:

(1) all planes perpendicular to the x-axis,

(2) all planes perpendicular to the y-axis,

and (3) all planes perpendicular to the line in the plane $y\,o\,z$ making an angle θ with the z-axis, where θ is given by

$$\tan\,\theta = \frac{b}{c} \qquad (1, 1)$$

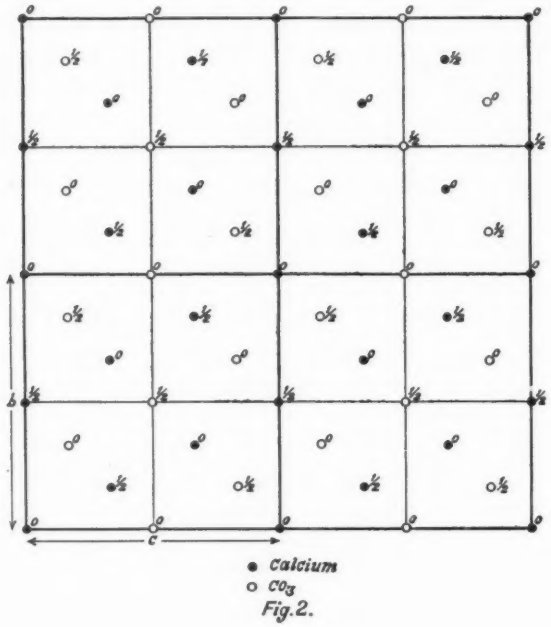


Fig. 2.

First System.—In this the distance between consecutive planes is given by

$$d = \frac{a}{2} \qquad (1, 2)$$

In a unit cell of each neutral plane, there are six lattice-points. Fig. 3 shows the arrangement of the ions in the planes at $x = \mathrm{O}, \pm a, \pm 2a, \ldots . \pm na, \ldots .$

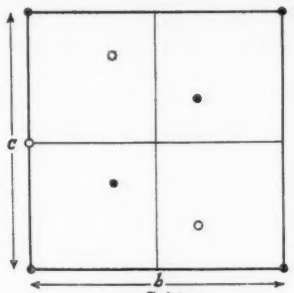


Fig.3.

The y and z co-ordinates of the 6 lattice-points are given by

$$\left.\begin{array}{llll} k=1, \text{ calcium ion } \left(0,\ 0\right); & k=4, \text{ } CO_3 \text{ ion } \left(0,\ \frac{c}{2}\right) \\ k=2, \quad ,, \quad ,, \left(\frac{b}{3},\ \frac{c}{3}\right); & k=5, \quad ,, \quad ,, \left(\frac{b}{3},\ \frac{5c}{6}\right) \\ k=3, \quad ,, \quad ,, \left(\frac{2b}{3},\ \frac{2c}{3}\right); & k=6, \quad ,, \quad ,, \left(\frac{2b}{3},\ \frac{c}{6}\right) \end{array}\right\} \qquad (1,\ 3)$$

The ionic arrangement in the planes at

$$x = \pm\frac{a}{2}, \pm\frac{3a}{2}, \cdots \pm\frac{2n+1}{2}\ a, \cdots$$

is similar to this except that there is a displacement of the ions through a distance $\frac{b}{2}$ along Oy.

Second System.—In this the distance between consecutive planes is given by

$$d = \frac{b}{6} \qquad (1,\ 4)$$

The unit cell of each plane consists of only two lattice-points.

Fig. 4 shows the arrangement of the ions in the plane $y = 0$. The x and z co-ordinates of the lattice-points are

$$k = 1, \text{ calcium ion } (0,\ 0) \text{ and } k = 2, \text{ } CO_3 \text{ ion } \left(0,\ \frac{c}{2}\right) \qquad (1,\ 5)$$

The successive planes are similar in the ionic arrangement except that each is displaced through distances $\frac{a}{2}$ and $\frac{2c}{3}$ along Ox and Oz respectively.

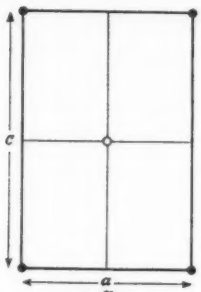


Fig. 4.

Third System.—In this the distance between consecutive planes is given by

$$d_\theta = \frac{bc}{2\sqrt{b^2+c^2}} \qquad (1, 6)$$

For the representation of this system we choose a system of co-ordinates x_θ, y_θ, z_θ; such that Ox_θ coincides with Ox and Oz_θ is perpendicular to the system of parallel planes. The dimensions of a unit cell of the plane lattice are given by

$$\left.\begin{aligned} a_\theta &= a \\ b_\theta &= \frac{\sqrt{b^2+c^2}}{3} \end{aligned}\right\} \qquad (1, 7)$$

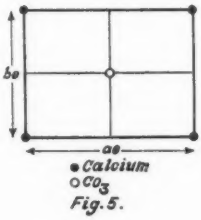


Fig. 5.

Fig. 5 shows the arrangement of the ions in the plane $Z_\theta = 0$. A unit cell of the lattice consists of two points only, whose x_θ and y_θ co-ordinates are given by

$$k = 1, \text{ calcium ion } (0, 0); \; k = 2, \text{ } CO_3 \text{ ion } \left(\frac{a_\theta}{2}, \frac{b_\theta}{2}\right); \qquad (1, 8)$$

The ionic arrangement in successive planes is similar except that each is displaced through distances $\frac{a_\theta}{2}$ and $\frac{b_\theta}{4}$ along Ox_θ and Oy_θ respectively.

Denoting the elasticity constants in directions perpendicular to these three systems by c_{11}, c_{22} and c_{33}^{θ} respectively; we have as in II (1, 9)

$$\left.\begin{aligned} c_{11} &= c_{11}^{e} + c_{11}^{r} \\ c_{22} &= c_{22}^{e} + c_{22}^{r\theta} \\ \text{and } c_{33}^{\theta} &= c_{33}^{e} + c_{33}^{r\theta} \end{aligned}\right\} \qquad (1, 9)$$

§2. *Evaluation of* c_{11}^{e}, c_{22}^{e} *and* c_{33}^{e}.

As derived in II (2, 12) we have

$$c_{11}^{e} = \frac{4\pi^2}{b^2c^2}\, 4e^2 \sum_{j=1}^{\infty} \left\{ \frac{\alpha_{l,m} \mid jd \mid}{2\pi}\; e^{-\alpha_{l,m} \mid jd \mid} \sum_{k} [\mathrm{F}_{l}^{l,m}(k)] \right\} \qquad (2, 1)$$

where

$$\alpha_{l,m} = 2\pi \left| \frac{l}{b} + \frac{m}{c} \right| \qquad (2, 2)$$

The function $\mathrm{F}_{l}^{l,m}(k)$ depends, as shown in II [§2, refer equation (2, 5) — (2, 10)] on the ionic arrangement of the planes.

The functions $\alpha_{l,m}$ and $\mathrm{F}_{l}^{l,m}$ will be different in the 3 cases.

In the first system, only two adjoining planes need to be considered. The bracketed expression on summation is found to be

$$-0{\cdot}267\,; \qquad (2, 3)$$

In the second case, only five adjoining planes have to be considered.

$$-0{\cdot}085\,; \qquad (2, 4)$$

In the third case, the summation yields the value

$$-0{\cdot}1048\,; \qquad (2, 5)$$

Substituting these in the proper formula we get

$$c_{11}^{e} = \frac{16\pi^2e^2}{b^2c^2}(-0{\cdot}267) = -0{\cdot}176 \times 10^{12}\ \text{dynes/cm.}^2\,; \qquad (2, 6)$$

$$c_{22}^{e} = \frac{16\pi^2e^2}{c^2a^2}(-0{\cdot}085) = -0{\cdot}169 \times 10^{12}\ \text{dynes/cm.}^2\,; \qquad (2, 7)$$

and

$$c_{33}^{e\theta} = \frac{16\pi^2e^2}{a_\theta^2 b_\theta^2}(-0{\cdot}1048) = -0{\cdot}916 \times 10^{12}\ \text{dynes/cm.}^2\,; \qquad (2, 8)$$

§3. *The Nature of the Repulsive Forces.*

The change in the potential due to the repulsive forces is given by III (2, 1)

$$2\,\frac{\beta}{\delta^n}\,; \qquad (3, 1)$$

where, as in I (3, 4)

$$\beta = \frac{ae^2}{n}\,\delta^{n-1}\,; \qquad (3, 2)$$

δ is defined in III (1, 24).

The force between two dissimilar ions is $\frac{b_{12}}{r^n}$ and $\frac{b_{11}}{r^n}$ or $\frac{b_{22}}{r^n}$ between two similar ions. Let

$$b_{11} = b_{22} = -kb_{12}\,; \tag{3, 3}$$

As in II (§3) we consider only the close neighbours of any ion ; in fact we take only such neighbours of which the distances from the ions are less than δ, defined in III (1, 24) . Further from III (1, 1) we get

$$b = 8{\cdot}63 \tag{3, 4}$$

Thus b may be taken roughly equal to c. Putting

$$\left.\begin{array}{ll} r_1^2 = \frac{b^2}{4}\,; & s_1^2 = a^2\,; \\ r_2^2 = b^2\left(\frac{1}{9} + \frac{1}{3\cdot6}\right); & s_2^2 = b^2\left(\frac{1}{9} + \frac{1}{9}\right); \\ r_3^2 = b^2\left(\frac{4}{9} + \frac{1}{3\cdot6}\right); & s_3^2 = b^2\left(\frac{1}{9} + \frac{4}{9}\right); \\ r_4^2 = b^2\left(\frac{1}{3} + \frac{1}{4}\right); & \end{array}\right\} \tag{3, 5}$$

The potential due to the repulsive forces is given by

$$V_\triangle = 12\, b_{12}\left\{\frac{2}{r_1^n} + \frac{6}{r_2^n} + \frac{6}{r_3^n} + \frac{12}{r_4^n} - k\left(\frac{6}{s_1^n} + \frac{6}{s_2^n} + \frac{12}{s_3^n}\right)\right\} \tag{3, 6}$$

n has been found in III (Table II) to be 6·5.

Expressing the distances in terms of δ

$$V_\triangle = \frac{12\, b_{12}}{\delta^{6.5}}\{1275{\cdot}6 - 332\,k\} \tag{3, 6'}$$

Comparing this with (3, 1)

$$\frac{2\,ae^2\,\delta^{5.5}}{6{\cdot}5} = 12\, b_{12}\,(1275{\cdot}6 - 332\,k) \tag{3, 7}$$

whence

$$b_{12} = \frac{a\,e^2\,\delta^{5.5}}{6 \times 6{\cdot}5\,(1275{\cdot}6 - 332\,k)} \tag{3, 8}$$

Substituting this in (3, 6)

$$V_\triangle = 2\,\frac{ae^2\,\delta^{5.5}}{6{\cdot}5\,(1275{\cdot}6 - 332\,k)}\left\{\frac{2}{r_1^{6.5}} + \frac{6}{r_2^{6.5}} + \frac{6}{r_3^{6.5}} + \frac{12}{r_4^{6.5}} - k\left(\frac{6}{s_1^{6.5}} + \frac{6}{s_2^{6.5}} + \frac{12}{s_3^{6.5}}\right)\right\} \tag{3, 9}$$

V, the potential per unit volume, is given by

$$V = \frac{V_\triangle}{\delta^3} \tag{3, 10}$$

For c_{11}^r, c_{22}^r and $c_{33}^{r\theta}$ we take formula similar to those given in II (3, 11) and (3, 12).

The value of k is determined, as in the case of aragonite, by comparison with the observed value of c_{11}.

§4. *Evaluation of* k *and* $c^r_{zz}\theta$.

Carrying out the differentiations and then substituting the numerical values of the r's and s's and their components in the respective directions we get :—

$$c^r_{11} = \frac{a e^2}{\delta^4} \frac{1870 \cdot 3 - 363 \cdot 8\, k}{1275 \cdot 6 - 332\, k} \tag{4, 1}$$

$$c^r_{22} = \frac{a e^2}{\delta^4} \frac{1870 \cdot 3 - 363 \cdot 8\, k}{1275 \cdot 6 - 332\, k} \tag{4, 2}$$

$$c^r_{33}\theta = \frac{a e^2}{\delta^4} \frac{2478 \cdot 6 - 455 \cdot 1\, k}{1275 \cdot 6 - 332\, k} \tag{4, 3}$$

From (4, 1) and (4, 2)

$$c^r_{11} = c^r_{22}$$

and since from (2, 6) and (2,7) we have c^r_{11} and c^r_{22} approximately equal, we obtain by calculation the observed result

$$c_{11} = c_{22} \tag{4, 4}$$

The value of c_{11}, as experimentally determined by Voigt,[2] is $1 \cdot 37 \times 10^{12}$ dynes/cm.^{2}

Hence from (1, 9) and (2, 6)

$$c^r_{11} = 1 \cdot 546 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 5}$$

$$\therefore \quad \frac{a e^2}{\delta^4} \frac{1920 \cdot 8 - 327 \cdot 8\, k}{1215 \cdot 6 - 332\, k} = 1 \cdot 546 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 6}$$

Substituting the proper values of e and δ, and the value of a from III (1, 28) we get

$$1 \cdot 03 \frac{1870 \cdot 3 - 363 \cdot 8\, k}{1275 \cdot 6 - 332\, k} = 1 \cdot 546 \tag{4, 7}$$

whence

$$k = 0 \cdot 353 \tag{4, 8}$$

Substituting this value of k in (4, 3)

$$c^r_{33}\theta = 2 \cdot 06 \cdot \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 9}$$

The value of the elasticity constant in the direction Oz_θ is not directly measured. As in II (5, 1) this can be obtained with the transformation formula given by Voigt. We get

$$c^\theta_{33} = 1 \cdot 109 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 10}$$

Substituting from (4, 9) and (2, 8) in (1, 9) the calculated value is given by

$$c^\theta_{33} = 1 \cdot 148 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 11}$$

The agreement between the two values is quite satisfactory.

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[2] W. Voigt, *Lehrbuch der Kristallphysik*, p. 754.

Summary.

The electro-static parts of the elasticity constants c_{11}, c_{22} and c_{33}^{θ} are calculated by the same method as used for aragonite. The nature of the 'repulsive' forces is further completely determined by comparison with the observed value of c_{11}. The value of c_{33}^{θ} is then determined and found to agree well with the experimental value.

REFRACTIVE INDICES AND DISPERSIONS OF GASES AND VAPOURS.

Substituted Methanes and Ethane, Cyclopropane, Ethylene Oxide and Benzene.

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In a previous paper,[1] the dielectric coefficients of the above-mentioned gases and vapours at different temperatures have been given. Results of refractive indices and dispersions of the same samples of materials form the subject of this communication.

Many of the substances investigated are liquids at the ordinary temperatures and therefore have very low vapour pressures. Consequently measurements had to be carried out at extremely small pressures to avoid spurious results due to effects of adsorption. But then the difficulties in determining the values of compressibilities were considerable. In order to arrive at fairly reliable results several additional precautions were taken. The pressures were read with greater accuracy using a micrometer eye-piece. Repeated measurements with the mercury meniscus rising and falling were made and the zero reading in each case was checked at the end of a count.

The apparatus, method of measurement, and the general procedure adopted were in essence similar to those described in the earlier papers.[2] Slight modifications, however, were made for introducing and purifying the vapours, particularly those of high boiling liquids. In some experiments, the original tubes with ground ends were replaced by a new set of identical tubes having extensions which could be sealed on to the main apparatus. This had an additional advantage in that, the effects of adsorption and in some cases of decomposition at the wax joints were completely removed. After each measurement, the apparatus was evacuated with a hyvac cenco pump, warmed slightly and washed several times with dry air. The apparatus was then left in the evacuated condition for two to three days and the

[1] K. L. Ramaswamy, *Proc. Ind. Acad. Sci.*, A, 1936, **4**, 108.

[2] H. E. Watson and K. L. Ramaswamy, *Proc. Roy. Soc.*, A, 1936, **156**, 144-57; *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 360.

traces of desorbed gases removed. Before conducting a new series with another substance, the tubes were once or twice washed with the vapour of the material and thoroughly evacuated and dried.

Compressibility.

In spite of all the precautions taken the values of compressibility could not be determined with great accuracy for vapours of substances which are liquids at the ordinary temperature. A few measurements carried out at the beginning of the series using pressures near to the saturation pressures, indicated that in many cases the compressibility was not a linear function of pressure but indicated a rapid rise up to a certain limit, then decreased and thereafter remained more or less steady. The curves obtained resembled those of adsorption at a surface. Probably the effects of adsorption were considerable even at such pressures. It was, however, not possible to say whether it was solely due to changing compressibility or due to combined effects of changing compressibility and adsorption.

Later on the measurements were repeated at lower pressures far removed from the saturation pressures at the prevailing temperatures and as before the values of dn/dp (dn is the number of bands for a difference of pressure dp) were plotted against the mean pressures. The points lay more or less on a straight line from which the factor and the compressibility could be calculated as mentioned in the earlier papers.[2] The whole numbers of bands were then determined for all the wave-lengths. From each set of figures under each wave-length, the compressibility was determined as in the case of the counts for the green line of mercury. The mean of the five values was then taken, the pressures recorrected and the values finally were recalculated.

In the case of substances which are gases at the ordinary temperatures, the usual procedure was adopted employing high pressures and no difficulty was experienced in getting accurate values for compressibility.

Preparation and Purification.

The details regarding the methods of preparation and purification of the materials have already been dealt with in the earlier publication.[1]

Results.

Table I gives the values of refractive indices for the five wave-lengths employed, the calculated values of C and ν_0^2 in the Sellmeir dispersion formula, and the extrapolated value of $n - 1$ obtained by dividing C by ν_0^2. For the sake of uniformity, the constants C and ν_0^2 have been calculated from the values for the mercury green and violet lines. Just below the values of $n - 1 \times 10^6$ are given the differences between the observed and the calculated values for the three other wave-lengths. All the figures represent what they

TABLE I.

Values of $n - 1_{25^\circ\cdot0\,C.}^{760\ mm.} \times 10^6$ *and Differences (calc.—obs.)* $\times 10^8$.

Wave-length	6440·24	5462·25	5087·23	4801·25	4359·56	C $\times 10^{-27}$	$\nu_0^2 \times 10^{-27}$	$C/\nu_0^2 \times 10^6$
CH_3F ..	403·46 −4	405·97	407·36 +1	408·66 +2	411·24	5·44004	13701·44	397·04
CH_3Cl ..	700·60 −9	706·15	709·25 +1	712·12 +4	717·88	7·42118	10810·70	686·47
CH_3Br ..	863·60 −4	872·08	876·74 +5	881·12 +8	889·91	7·47438	8872·10	842·46
CH_3I ..	1167·57 −55	1183·03	1191·66 +28	1199·88 +42	1216·93	7·29266	6465·74	1127·89
CH_3NH_2 ..	620·64 −20	626·10	629·08 +15	631·98 +16	637·91	5·80732	9576·73	606·40
CH_3CN ..	690·43 −47	695·52	698·49 +10	701·54 −9	707·10	7·29297	10786·98	676·09
CH_3OH ..	512·09 −18	515·79	517·77 +16	520·01 −9	523·85	5·75665	11462·19	502·23
$(CH_3)_2O$ ..	807·33 +4	813·79	817·29 +4	820·66 −3	827·14	8·65830	10940·83	791·38
$(CH_2)_2CO$ ..	987·04 −25	995·57	1000·30 +12	1004·96 −1	1013·89	9·46150	9804·95	946·15
C_2H_5Cl ..	995·68 −13	1003·69	1008·16 +2	1012·38 −1	1020·64	10·37832	10641·51	975·27

TABLE I—(*Contd.*).

Wave-length	6440·24	5462·25	5087·23	4801·25	4359·56	$C\times10^{-27}$	$\nu_0^2\times10^{-27}$	$C/\nu_0^2\times10^6$
CH_2Cl_2 ..	1050·94 −5	1059·80	1064·75 −3	1069·32 −1	1078·37	10·56828	10273·30	1028·71
$CHCl_3$ ..	1314·85 −69	1325·02	1331·01 0	1336·48 +12	1347·63	13·56179	10536·50	1287·12
CCl_4 ..	1619·67 −119	1632·37	1640·27 −24	1647·41 −22	1661·31	16·09145	10159·07	1583·95
C_3H_6(*Cyclo*) ..	871·95 +4	879·24	883·24 0	887·06 −8	894·35	8·93666	10465·41	853·92
$(CH_2)_2O$ ..	682·18 −12	687·27	690·04 +10	692·79 +3	698·09	7·61438	11380·52	669·07
C_6H_6 ..	1606·49 −228	1627·80	1640·56 +39	1653·49 −19	1677·91	9·35987	6051·36	1546·74

would be had the gas or vapour been ideal. Since all the measurements were carried out in the neighbourhood of 25°·0 C., all the values have been calculated to 25°·0 C. and 760 mm. pressure. In the case of substances which are liquids at the ordinary temperature and pressure, the values at 760 mm. and 25°·0 C. appear meaningless since they do not exist as vapour under those conditions. As mentioned in an earlier paper,[1] they must be taken to represent what they would be if measured at 25°·0 C. and 760 mm. pressure.

In Table II, the values of compressibility have been repeated for the sake of convenience. For some substances the values mentioned here differ somewhat from those given in the earlier paper[1] and have either been obtained from later measurements or altered slightly to fit the dispersion fractions.

TABLE II.

Percentage compressibility corrections.

CH_3F	.. 1·07	CH_3OH	.. 4·7
CH_3Cl	.. 1·75	$(CH_3)_2CO$	.. 15·6
CH_3Br	.. 2·51	CH_3CN	.. 29·2
CH_3I	.. 4·69	$(CH_3)_2O$	.. 1·88
C_2H_5Cl	.. 3·25	CH_3NH_2	.. 2·93
CH_2Cl_2	.. 6·5	$(CH_2)_3$	.. 1·61
$CHCl_3$	.. 9·6	$(CH_2)_2O$	.. 2·81
CCl_4	.. 14·1	C_6H_6	.. 26·2

The figures in Table I show that in the case of several substances, the differences between the calculated and the observed values are quite appreciable particularly for the cadmium red line. Considering the enormous experimental difficulties, it is difficult to say whether they are due to errors in measurement or are real owing to the proximity of adsorption bands in the near infra-red. It is intended to investigate this question in greater detail at a later date.

Most of the substances mentioned in this paper have been investigated—though not in a systematic way—by Mascart, Prytz, Lorenz and Cuthbertson in the past and more recently by Lowery, Max Weiss, and others.

It appears, therefore, of interest to compare the results given in this paper with those of others, particularly in view of the fact that the methods employed by some differs essentially from the one adopted in these investigations. Table III gives a summary of most of the available data published so far.

For easy comparison all the values have been calculated to 25°·0 C. and a pressure of 760 millimetres for the wave-length 5894 Å. The author's figures for this wave-length have been obtained from the dispersion data given in Table I and are all corrected for compressibility. Results by others do not appear to have been corrected for compressibility in most cases. The wave-length 5894 Å has been particularly selected since it has been frequently employed in the past. All the values of $n-1\times10^6$ (where n represents the refractive index) in Table III are given to the nearest whole number.

A glance at the results in Table III shows that the results by different authors are in some cases extremely divergent. The discrepancies cannot always be attributed to impurities in the materials employed. Particularly in the case of vapours of high boiling substances, the question of adsorption has not been taken into account by earlier workers. This subject has been dealt with by Max Weiss in great detail in an important communication published nearly two years ago. It is not possible to go into the details of all the values given above. A few remarks, however, are necessary.

Cuthbertson has examined *methyl fluoride* but does not mention the details of measurement. The value does not appear to have been corrected for compressibility. Assuming that he has worked in the neighbourhood of 25°·0 C. and a pressure of 760 mm., and applying the correction for compressibility, the value comes out to be about 407, very near the observed value by the author.

Mascart's figures, are in general, higher than those given by others. Since he does not mention the sources of materials and the methods of purification, it is not possible to discuss about the results.

Prytz and Lorenz seem to have made the measurements with great care and their results are fairly in good agreement with the recent determinations. The value by Prytz for *benzene*, however, appears too low and it is possible that his specimen of the vapour contained air, which is very difficult to remove.

Wasastjerna has obtained in the case of *benzene* a value which is very close to that given by Mascart but is far higher than those given by both Max Weiss and the author. Max Weiss in a recent communication has discussed

TABLE III.

Values of $n-1_{25^\circ\cdot0\,C.}^{760\ mm.} \times 10^6$* *for* $\lambda = 5894$ Å.

	Author	C.	M.	P.	W.	L.	Lo.	Ma.	T.&K.	H.&G.
CH_3F ..	405	411	..	..	..	..	..	..	..	..
CH_3Cl ..	703	..	797	..	..	..	711	..	..	..
CH_3Br ..	868	..	883	..	..	..	..	..	..	..
CH_3I ..	1175	..	1166	1159	..	..	..	..	..	..
CH_3NH_2	623	..	..	..	..	..	..	..	..	..
CH_3CN..	693	..	711	..	..	..	..	..	..	..
CH_3OH ..	514	..	571	..	..	506	..	..	..	..
$(CH_2)_3O$	811	..	816	..	..	..	810	..	..	..
$(CH_2)_3CO$	991	..	1008	991	..	..	1001	..	..	..
C_2H_5Cl ..	1000	..	1080	..	..	..	..	992	..	..
CH_2Cl_2 ..	1055	..	..	..	..	..	1012	..	..	..
$CHCl_3$ ..	1320	..	1341	..	..	1321	1317 1321 (H.)	..	..	..
CCl_4 ..	1625	..	1630	..	..	..	1628	..	..	1630
$(CH_2)_3$ ..	876	..	..	..	..	..	..	..	895	..
$(CH_2)_2O$.	685	..	..	..	..	..	..	..	..	..
C_6H_6 ..	1616	..	1670	1562	1667	..	..	1620	..	..

* *Note*:

C. .. C. Cuthbertson, *Phil. Trans. Roy. Soc.*, 1905, **204**, 323.
M. .. Mascart, *C. R.*, 1878, **86**, 321, 1182.
P. .. K. Prytz, *Wied. Ann.*, 1880, **11**, 104.
W. .. Wasastjerna, *Soc. Scient. Fenn.*, 1924, **2**, No. 13, 24.
L. .. L. Lorenz, *Wied. Ann.*, 1880, **11**, 70.
Lo. .. H. Lowery, *Proc. Phys. Soc.*, 1927, **39**, 421-23; *ibid.*, 1927, **40**, 23-28; *Proc. Roy. Soc.*, A, 1931, **133**, 188-206.
L. & H. .. H. Lowery and T. S. Hartley, *Proc. Phys. Soc.*, 1931, **43**, 559-61.
Ma. .. Max Weiss, *Ann. Der. Physik*, 1934, **20**, 557.
T & K. .. Max Trautz and Karl Winkler, *Jour. pract. ch.*, 1922, **104**, 37.
H. & G. .. P. Hölemann and H. Goldschmidt, *Zs. anorg. chem.*, (B), 1934, **24**, 199-209.

the results of Wasastjerna and has concluded that the high values must have arisen from the effects of adsorption.

The results of Lowery are very close to the author's except in the case of *methylene chloride*. It was not possible to verify the results since the material was not available and therefore the data for this substance are given with reserve. Max Weiss has made a careful detailed investigation on *ethyl chloride* and *benzene* and has given the molar refractivities for $\lambda = 5461$ Å. He obtained a value of 3·8 per cent. for the compressibility of *ethyl chloride* at 20°·0 C. from refractometric studies. This value is comparable with the figure of 3·25 per cent. obtained by the author at 25°·0 C. employing the same method. For *benzene* he could not arrive at any value and he mentions that the results were viciated by the effects of adsorption. The figures 992 and 1620 for *ethyl chloride* and *benzene* respectively have been obtained from his results for 5461 Å assuming the dispersion obtained by the author and it may be mentioned that the values are in close agreement particularly for *benzene*.

Trautz and Winkler have measured the refractive index of *cyclopropane* for the helium yellow line but have not given the details of measurement. The same value has been reproduced after conversion to 25°·0 C., since the change in refractive index for 5894 Å would not be very much different from that for 5877 Å. Assuming as in the case of *methyl fluoride*, that the measurements have been made in the neighbourhood of 25°·0 C. and 760 mm. pressure, the value corrected for the compressibility comes to 879, which is fairly in agreement with the observed value of 876.

Carbon tetrachloride has been examined by several investigators and it is very satisfactory to note that the values by all are in satisfactory agreement. The most recent value is the one given by Hölemann and Goldschmidt, who have made the measurements at 180°C., at which temperature both the adsorption and the compressibility would be very small.

In Table IV, the results of electronic, distortion and atomic polarisation represented respectively by P_E, $P_E + P_A$, and P_A are given. The values of P_E have been calculated from the figures in the last column of Table I. The values of $P_E + P_A$ have been reproduced from the earlier paper.[1]

It has been already remarked in the previous paper,[1] that some substances gave either small or negative values for $P_A + P_E$. The negative values have no meaning or significance and might have arisen from errors in measurement of dielectric coefficients. The measurements of the latter were made only at two temperatures and the compressibilities obtained from refractometric studies were employed in correcting the values. In the case of gases

TABLE IV.

Values of $P_A + P_E$, P_E and P_A.

	$P_A + P_E$	P_E	P_A	$100\ P_A/P_E$
CH_3F ..	7·09	6·48	0·61	9·4
CH_3Cl ..	8·66	11·20	−2·54	..
CH_3Br ..	13·36	13·74	−0·38	..
CH_3I ..	18·65	18·39	0·26	1·4
C_2H_5Cl ..	15·21	15·90	−0·69	..
CH_2Cl_2 ..	18·74	16·78	1·96	11·7
$CHCl_3$ ..	24·92	20·99	3·93	18·7
CCl_4 ..	28·14	25·83	2·31	8·9
CH_3NH_2 ..	13·65	9·89	3·76	38·0
$(CH_2)_3$ ..	14·28	13·93	0·35	2·5
$(CH_3)_2O$ ..	15·03	12·91	2·12	16·4
C_6H_6 ..	27·43	25·22	2·21	8·8
CH_3OH ..	8·14	8·19	−0·05	..
$(CH_3)_2CO$ ..	6·0	15·43	−9·43	..
CH_3CN ..	−11·9	11·03	−22·93	..
$(CH_3)_2O$ ..	9·95	10·91	−0·96	..

the errors would be small and by taking a large number of readings, more accurate values of $P_A + P_E$ could be obtained. In the case of vapours of high boiling liquids, particularly when they are highly polar, the extrapolation of the dielectric polarisation to $1/T = 0$ from measurements at only two temperatures introduces considerable error. So far as the moment is concerned, it can be obtained with a fair degree of accuracy. It is intended, therefore, to repeat the measurements for some substances at different

intervals of temperature and thereby obtain more accurate values for the distortion polarisations.

However, it is interesting to mention that the atomic polarisation of *methyl fluoride* is comparatively small when compared with the values for other fluorides mentioned in the previous papers.[2] Another significant result is that of *methyl amine* for which the atomic polarisation is 38 per cent. of its electronic polarisation. Even for *chloroform* and *dimethyl ether* the values of atomic polarisations are fairly large.

Refractivity and Dispersion in Liquid and Vapour States.

The theories of the optical behaviour of liquids are, in general, based on the assumption that the well-known Lorentz formula $n^2 - 1/n^2 + 2 \cdot M/D =$ constant holds good for changes of temperature and pressure and for different states of aggregation. From the work of Fajans[3] and others it is evident that this relation is at best only an approximation. Taking the case of benzene Wasastjerna obtained values of refractivities 27·20 and 26·18 for the vapour and liquid for the sodium D line. Though this high value of 27·20 for the vapour has been attributed by Max Weiss to effects of adsorption, there is little doubt as to the indication that the vapour value should be higher than that of the liquid.

Investigations on light scattering have definitely shown that all known molecules are optically anisotropic, which means that the molecules are polarisable to different extents in different directions. From this point of view the refractivity of a liquid would be an average effect of the contributions of molecules variously orientated relatively to one another and to the field of incident radiation. From these and other considerations Raman and Krishnan[4] deduced an equation to explain the variation of refractivity from liquid to vapour.

It was therefore considered of interest to determine the refractivities of the liquids whose vapours also have been examined under known conditions and compare them with those for the vapours.

The refractive indices of the liquids were measured for two wave-lengths with the help of a Pulfrich refractometer using mercury arc as a source of light. The temperature was controlled by circulating water at constant temperature. All measurements were made at or nearly at the prevailing room temperature. The value of density at the temperature at which the refractive index and dispersion were measured, was obtained by interpolation

[3] Fajans, *Zeit. Physikal. Chem.*, B, 1934, **24**, 108.

[4] C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.*, A, 1928, **117**, 589; *ibid.*, 1930, **126**, 155.

from the values of density at different temperatures determined with the help of a specially constructed pyknometer.[2]

Table V contains the results of refractivities of the liquids and their corresponding vapours, the differences in refractivities in the two states and the dispersions expressed as the differences in $R_v - R_G$, where R_v and R_G represent the molar refractions for the mercury violet and green lines. The refractivities of the liquids have been calculated from the values of refractive indices and densities already given in the previous paper.[1]

TABLE V.

Refractivity and dispersion of liquids and vapours.

	$\lambda = 4359{\cdot}56$Å			$\lambda = 5462{\cdot}25$Å			Dispersion $R_V - R_G$	
	$R_{vap.}$	$R_{liq.}$	$R_{vap.}$-$R_{liq.}$	$R_{vap.}$	$R_{liq.}$	$R_{vap.}$-$R_{liq.}$	Liquid	Vapour
C_6H_6 ..	27·36	27·22	0·14	26·54	26·44	0·10	0·78	0·82
CCl_4 ..	27·09	27·05	0·04	26·62	26·57	0·05	0·48	0·47
$CHCl_3$ ..	21·98	21·86	0·12	21·60	21·49	0·11	0·37	0·38
CH_2Cl_2 ..	17·59	16·47	1·12	17·28	16·20	1·08	0·27	0·31
CH_3CN ..	11·53	11·37	0·16	11·34	11·20	0·14	0·17	0·19
CH_3I ..	19·85	..	..	19·29	19·45	−0·16	..	0·56
CH_3OH ..	8·54	8·39	0·15	8·41	8·26	0·15	0·13	0·13
$(CH_3)_2CO$	16·54	16·50	0·04	16·24	16·22	0·02	0·28	0·30

The tabulated values show that while the refractivities for the liquid and vapour states do not differ notably, the observed differences are always positive, indicating that in general, the value for the vapour state is slightly more than that for the liquid.

Regarding dispersion, it may be mentioned that the measurements are not so accurate as to ensure that the changes given in the table are real. Nevertheless the indications are that the dispersion in the vapours are slightly greater than in the corresponding liquids. Friberg[5] in a recent paper

[5] Friberg, *Z. Physikal. Chem.*, B, 1934, **26**, 195.

has come to the conclusion from his experiments that the dispersions in the liquid and vapour states are identical. Further investigations are necessary before this issue can be definitely decided.

Summary.

1. Refractive indices and dispersions have been measured for 16 gases and vapours using a Zeiss Interferometer of the Rayleigh type. Five wave-lengths 6440, 5462, 5087, 4801 and 4360 have been employed for the purpose.

2. Accurate values of compressibilities for the gases and approximate values for the vapours have been obtained by studying the variation of refractive index with pressure.

3. The electronic polarisation obtained in this paper have been compared with the dielectric polarisations given in the earlier paper[1] and from the two the atomic polarisations have been calculated.

4. The values of refractive index for the gases and vapours by the author have been compared with existing data by others and discussed.

5. Refractivities in the liquid state for substances which are liquids at the ordinary temperature and pressure were measured for two wave-lengths using a Pulfrich Refractometer and a mercury arc. These values have been compared with those obtained for the corresponding vapours.

6. The results show that in general the refractivities of the vapours are slightly higher than those of the liquids.

7. The dispersions in the liquid and vapour states have been compared. The indications are that the values in the vapours are slightly higher than in the corresponding liquids.

In conclusion, I wish to express my best thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work.

THE DIPOLE MOMENT AND STRUCTURE OF PYRONES.

2·6 Dimethyl-γ-Pyrone, Xanthone and Coumarin.

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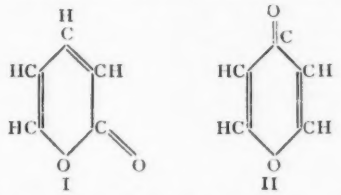
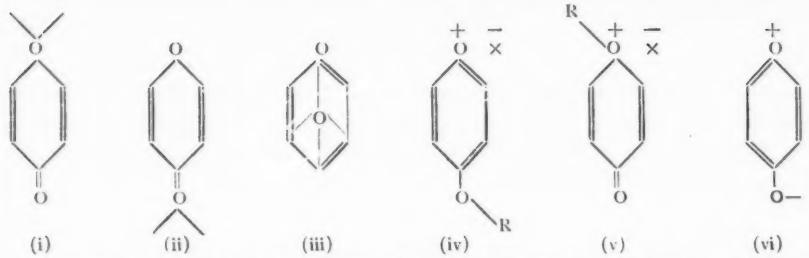
The pyrones are an important class of organic compounds containing a six membered heterocyclic ring of five carbon atoms and one oxygen atom, one of the carbon atoms having formed a ketonic group. There are two isomeric forms possible, the α-pyrones and the γ-pyrones, whose constitutional formula in which the atoms exhibit normal co-valencies are I and II respectively.



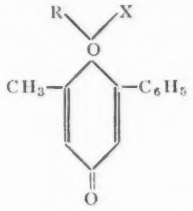
The commonest representative of an α-pyrone is benzo-α-pyrone or coumarin, the aromatic principle of wood-ruff and other plants : the γ-pyrones on the other hand are found even more extensively in nature as yellow colouring matters and also in opium. A special feature of the properties of all these pyrones, is that the carbonyl groups present in them do not exhibit their usual chemical reactivity such as the formation of oximes and phenyl hydrazones. An even more marked feature is a feeble basicity which they exhibit and build as a consequence a number of characteristic salts. These properties of the pyrone-ring have been the subject of considerable interest for a long time and a variety of investigations on the chemical and physical properties of these compounds have resulted, until recently, in the formulation of several different structures, on none of which however there has been a general agreement.[1] All these formula can, in general, be grouped into (i) those in which the ring oxygen atom alone exhibits quadrivalency, (ii) those in which the carbonyl oxygen alone exhibits quadrivalency, (iii) those in which both oxygen atoms exhibit quadrivalency and a whole series of other formula (iv), (v), (vi) according to which the pyrones form co-ordination compounds.

[1] Beilstein, *Handbuch der Organische Chemie*, 4th Edition, Band XVII, 1933, p. 268.

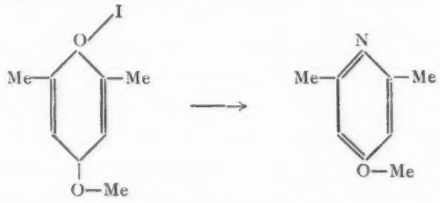


(i) (ii) (iii) (iv) (v) (vi)

Among some of the elegant experiments in favour or against any of these formulæ may be mentioned the observation of Gibson and Simonsen[2] about the non-resolvability of 2 phenyl 6 methyl-4-pyrone-*d* α-camphor sulphonate



thus disproving formula (i), and the experiment of Bayer[3] by which the methiodide of dimethyl-γ-pyrone could be readily transformed to methoxy lutidine and so must be represented by formula (iv).



The evidences provided in this connection by the study of the absorption spectra of pyrones and their salts have been rather indefinite.[4] An elimination of a number of these hypothesis, and a definite orientation of ideas has been possible since the advent of the electromeric theories of structure developed by Robinson,[5] and the quantum-mechanical resonance theory

[2] C. S. Gibson and J. L. Simonsen, *Jour. Chem. Soc.*, 1928, 2307.

[3] A. Bayer, *Ber.*, 1910, **43**, 2337.

[4] A. A. Boon, F. J. Wilson and I. M. Heilbron, *Jour. Chem. Soc.*, 1914, **105**, 2177. A. Hantsch, *Ber.*, 1919, **52**, 1535. R. C. Gibbs, J. R. Johnson and E. C. Hughes, *Jour. Amer. Chem. Soc.*, 1930, **52**, 4895.

[5] R. Robinson, *Outline of an Electrochemical Theory of Course of Organic Reactions.* Institute of Chemistry Lecture, 1932.

of molecular structure developed by Pauling,[6] and it is now definitely considered that the true state of the pyrone molecule is an intermediate one between the ketonic and the betain-like ionised form (vi).[7] A considerable support to this view has been provided by the dipole moment measurements of Partington,[8] who found for dimethyl γ-pyrone a moment value much higher than that calculated for the usual ketonic formula. The object of the present investigation is to verify and more fully interpret these dipole moment measurements for a series of similar compounds.

Experimental.

The moments were measured by the method of dilute solutions, using benzene as solvent, and over a range of 10° to 40° C. The test condenser used in the dielectric constant measurements, the methods of filling and handling the same, were exactly as described in a previous paper,[9] excepting that the capacities were measured in a heterodyne apparatus, instead of in the bridge circuit previously employed. In the present apparatus, a screened-grid valve oscillator was employed, and it was stabilised as described by Schweimer and Pungs[10] by adjusting the ratio between the screened-grid and anode voltages to an optimum value. It has been shown that such an oscillator can maintain the frequency constant for a wide range of frequencies, and that even changes in anode voltage by 50% and in heating current by 20% cause only a change of 20 cycles in 2 millions. The diagram of the circuits is given in Fig. 1.

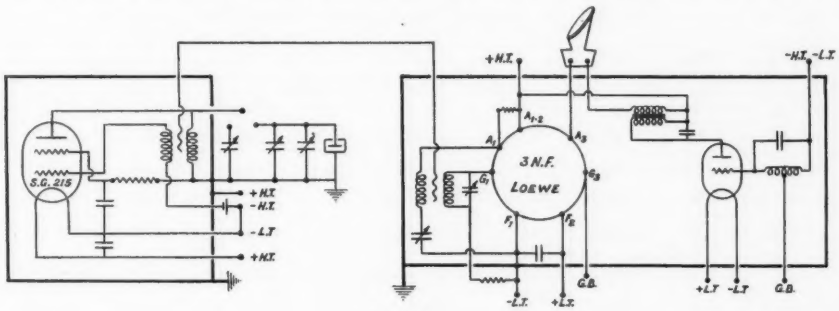


FIG. 1.

[6] L. Pauling and J. Sherman, *Jour. Chem. Phys.*, 1933, **1**, 605.
L. Pauling, L. O. Brockway and J. Y. Beach, *Jour. Amer. Chem. Soc.*, 1935, **57**, 2705.
[7] F. Arndt and B. Eistert, *Zeit. Physik. Chem.*, (B), 1935, **31**, 125.
[8] E. C. E. Hunter and J. R. Partington, *Jour. Chem. Soc.*, 1934, 87.
F. Arndt, G. T. O. Martin and J. R. Partington, *ibid.*, 1935, 602.
[9] M. A. Govinda Rau and B. N. Narayanaswamy, *Zeit. Physik. Chem.*, (B), 1934, **26**, 23.
[10] K. P. Schweimer and L. Pungs, *Hochfrequenztechn und Elektroak.* 1934, **43**, 181.

The beat oscillator and amplifier were built round a Loewe 3NF valve, and this together with a triode audio-frequency tuner was enclosed in one screened box. The calibrated main and vernier condensers, of capacities 1000$\mu\mu$F and 80$\mu\mu$F respectively, were arranged outside the screened-grid oscillator box, and the high tension leads were shielded by concentric tubular earthed return conductors, so as to reduce the stray capacity effects to a minimum. The constancy of the beat oscillator through the experiment was checked by switching over the screened-grid oscillator coils to an auxiliary variable condenser which was left fixed and undisturbed throughout the measurements. The apparatus worked with a remarkably constant frequency.

The densities of solutions were measured with a U-shaped dilatometer and the calculations of molecular polarisations at infinite dilution $P_{2\infty}$ at 10°, 20°, 30° and 40° C. were carried out by adopting the Hedestrand method as described already.[9]

The solvent benzene was a thiophen-free sample which was carefully dried over phosphorous pentoxide and redistilled twice in an all glass apparatus before use. All the specimens of solutes employed were "pure" as supplied by Kahlbaum and were recrystallised from distilled benzene or alcohol as the case may be, until the melting points were constant and tallied with the accepted values.

Results.

The results are given in Tables I, II and III.

TABLE I. 2·6 *Dimethyl γ-Pyrone.*

Concentration of solute in mol fraction	10°C.		20°C.		30°C.		40°C.	
	E	d	E	d	E	d	E	d
0	2·299	0·8884	2·280	0·8777	2·261	0·8669	2·242	0·8561
0·00531	2·469	0·8899	2·442	0·8792	2·415	0·8685	2·387	0·8577
0·01057	2·633	0·8913	2·598	0·8807	2·563	0·8701	2·529	0·8596
0·01108	2·640	0·8913	2·605	0·8807	2·570	0·8701	2·535	0·8596
0·01492	2·765	0·8924	2·724	0·8819	2·682	0·8713	2·641	0·8608
0·01967	2·908	0·8938	2·862	0·8833	2·816	0·8727	2·770	0·8621

	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10°	30·64	0·273	470·9	4·47
20°	29·20	0·284	459·1	4·48
30°	27·98	0·292	449·7	4·51
40°	26·64	0·307	437·8	4·51

(P_E = 36·0)

TABLE II. *Xanthone.*

Concentration of solute in mol fraction	10°C.		20°C.		30°C.		40°C.	
	E	d	E	d	E	d	E	d
0	2·298	0·8880	2·279	0·8773	2·260	0·8665	2·240	0·8558
0·00559	2·377	0·8918	2·354	0·8812	2·332	0·8705	2·309	0·8598
0·01024	2·443	0·8950	2·418	0·8844	2·392	0·8737	2·366	0·8630
0·01579	2·518	0·8988	2·490	0·8881	2·461	0·8775	2·433	0·8669

	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10°	13·92	0·683	244·9	2·91
20°	13·36	0·683	240·9	2·93
30°	12·77	0·699	235·5	2·94
40°	12·23	0·701	231·2	2·95

(P_E = 60·0)

TABLE III. *Coumarin.*

Concentration of solute in mol fraction	10°C.		20°C.		30°C.		40°C.	
	E	d	E	d	E	d	E	d
0	2·299	0·8881	2·279	0·8774	2·260	0·8667	2·241	0·8560
0·00599	2·490	0·8909	2·462	0·8803	2·434	0·8697	2·406	0·8591
0·00918	2·590	0·8926	2·558	0·8821	2·525	0·8715	2·493	0·8609
0·01440	2·757	0·8949	2·716	0·8845	2·676	0·8740	2·635	0·8635
0·01748	2·856	0·8967	2·811	0·8861	2·766	0·8755	2·721	0·8650

	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10°	31·86	0·482	489·7	4·50
20°	30·36	0·488	477·6	4·51
30°	28·97	0·504	465·7	4·52
40°	27·45	0·514	451·4	4·52

(P_E = 43·0 + 5·5 ± 48·5)

The only previous determination of the moment of 2.6 dimethyl-γ-pyrone was made by Hunter and Partington,[8] but their values are considerably lower than those presented here. At 20°·0 C. the temperature at which all their measurements have been made, the $P_{2\infty}$ and moment values are 385 c.c. and $4·05 \times 10^{-18}$ e.s.u. respectively. The value for $P_{2\infty}$ is thus lower by 74 c.c. An attempt at recalculating $P_{2\infty}$ from their published data, adopting

the Hedestrand method, could not be carried through, as no satisfactory straight line could be drawn through the dielectric constant and density points when plotted against the molar concentration. The nearest value for a, the dielectric constant slope, was only 26·1 as against 29·2 obtained in the present experiments, and thus the difference in the values of the slope a alone accounts for 52 c.c. of the discrepancy between our results.

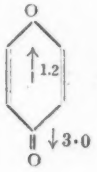
On account of the high moment of the molecule, the effect, on the $P_{2\infty}$ of the solute, of the decrease in dielectric constant with rise in temperature, has been noticeable, and no straight line could be drawn through the $P_{2\infty}$ points plotted against the reciprocal of the absolute temperature.[11] The same solvent effect could also be observed in the case of xanthone and coumarin.

For xanthone a moment of 3·07 has been reported by Bergmann and Weizmann.[12] This is in fair agreement with the present data. The value of electronic polarisation P_E used in the calculation of moment, was computed from the atomic refractivities and rounded off to 60·0 to take into account the atomic polarisations.

For coumarin no previous data have been reported. The P_E value has been taken from Anderlini's[13] determinations.

Discussion.

From the usual concepts of stereochemistry, and the magnitudes of the co-valency angles one should expect the pyrone-ring with its two double bonds to be a plane structure, with all the ring atoms and those directly attached to them in the same plane. As the two moment centres in the ring, the ethereal oxygen and the carbonyl group, are separated into the *para* positions, any inductive reaction between them will be negligible, and the moment of the molecule can be calculated as the difference between the two group moments as in Fig. 2.



$= 3{\cdot}0 - 1{\cdot}2 = 1{\cdot}8 \times 10^{-18}$ e.s.u.

FIG. 2.

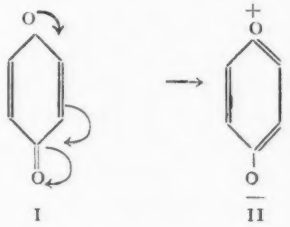
Now, since 2.6 dimethyl-γ-pyrone and xanthone can be regarded as symmetrically substituted γ-pyrones, their moments must be equal and have the

[11] M. A. Govinda Rau and B. N. Narayanaswamy, *Proc. Ind. Acad. Sci.*, 1935, **1**, 489.
[12] E. Bergmann and A. Weizmann, *Trans. Far. Soc.*, 1936, **32**, 1327.
[13] F. Anderlini, *Gazz. Chim. Ital.*, 1895, **25**, ii, 142.

same value 1·8.† The observed values of 4·5 and 3·9 for these molecules are in the first instance not equal, and secondly they are both considerably higher than the calculated value. As already referred to, this has been explained as essentially due to the presence of a highly polar excited state for these molecules. The capacity of such molecules to exhibit this state is very interesting, and a regular study of this phenomenon is of great importance in elucidating the reactivities of molecules. The concept originated on the chemical side from attempts to correlate the characteristic aromatic reactions in *ortho*, *meta* and *para* substitutions, and the special properties of conjugated double bonds in transmitting polar effects. The mechanism of this change to excited states has been called by Robinson[5] electromerism, and he has given a full and connected account of these phenomena. It is a fact of general observation that when an oxygen atom is singly linked to an unsaturated carbon atom, it tends to donate one of its unshared electrons and thereby increase its co-valency with the carbon atom, the oxygen atom becoming in this process a seat of positive charge : thus

On the other hand, if the oxygen atom is doubly linked with the same carbon atom as in $-\overset{\curvearrowright}{C}=O$, the tendency is for the co-valency to decrease by the oxygen accepting one of the carbon electrons, and becoming a seat of negative charge : thus

When both types of oxygen atoms are present as in the γ-pyrones, this tendency for the shift of electrons is considerably favoured and the molecule exhibits a more or less permanent displacement and therefore polarity. In the case of γ-pyrone the electromeric change is given by formula II.



I II

† All moment values are given in units of 10^{-18} e.s.u.

The moment of this valency isomer will be approximately $4{\cdot}77 \times 10^{-10} \times 3 \times 1{\cdot}5 \times 10^{-18} = 22 \times 10^{-18}$ e.s.u. (neglecting the co-valency moments). The substance is not however to be regarded as a mixture of these two types of molecules existing in dynamic isomerism ; on the other hand, every molecule is in the identical state, intermediate between the two extremes. Indeed, the moment of such a molecule is not the mean square of the moments of the various unperturbed states, with a value numerically between, but is always a vectorial mean among the values. Thus if the moment of the excited state is in the opposite sense to that in the normal molecule, the actual moment of the molecule will be lower than that calculated for the normal state. These conceptions of electron degeneracy in conjugated systems have been studied by Pauling[6] from the view-point of quantum-mechanics and he has shown that such molecules exist in a state of resonance between two or more valence bond structures, each structure having a definite contribution to make towards the actual state of the molecule. Thus if a molecule can be represented by $\psi = a_1\psi_1 + a_2\psi_2$ where $a_1^2 + a_2^2 = 1$, and a_1 and a_1 are the coefficients for the excited states ψ_1 and ψ_2, and, if the moments of these parent states along the x-axis are μ_{1x} and μ_{2x} respectively, then the moment of the hybrid state along this axis will be[14]

$$\mu = e \int_{-\infty}^{+\infty} \psi^* \left(\sum_{i=1}^{n} x_i - a \right) \psi \, d\tau$$

$$= a_1^2 \mu_{1x} + a_2^2 \mu_{2x} + 2 a_1 a_2 e \int_{-\infty}^{+\infty} \psi_1^* \left(\sum_{i=1}^{n} x_i - a \right) \psi_2 \, d\tau$$

Here e is the electronic charge, a the x-co-ordinate of the centroid of positive charge, and the suffix i refers to the ith electron, there being n in all. In this expression for the moment the third term is a cross term, which though not negligible, is probably considerably less than the sum of the first two terms. Accordingly we may form a rough idea of the coefficients of the structures, if we know only the three moments. In the case of dimethyl γ-pyrone, assuming but a single excited state with $\mu = 22{\cdot}0$, the moment being in the same direction as in the normal co-valent molecule, a simple calculation gives the contribution of the excited state to the moment of the molecule to be 15%. However, such simple calculations cannot always be carried out as the moments of the excited states may be in several different directions and vectorial methods must then be used.

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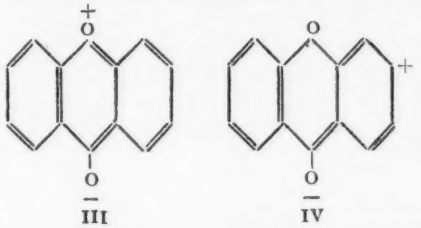
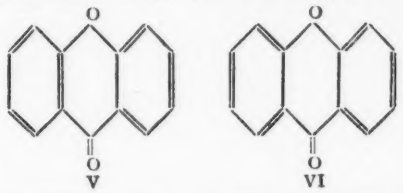
[14] L. E. Sutton, *Trans. Far. Soc.*, 1934, **30**, 793.

In the case of xanthone with two benzene rings fused on to the pyrone nucleus, there are more than one of these " non-orthogonal excited canonical states " possible, each with a high moment value as in III and IV



III IV

but, in addition to these, there are also a number of unexcited canonical states such as V and VI, each with the low co-valency dipole moment value of 1·8



V VI

units. The presence of these latter will tend to diminish the contribution of the excited states. The moment of xanthone is therefore less than that of γ-pyrone. The moment of chromone, which is benzo-γ-pyrone, has not yet been determined, but its value must be between those of dimethyl-γ-pyrone and xanthone, if only because of the fewer number of unexcited states contributing to the resonant state than in xanthone. The observed smaller dipole moment of 2.6-diphenyl-γ-pyrone,[15] *viz.*, 3·82, could also be explained on exactly similar grounds.

The dipole moment of coumarin is another highly interesting value.[16] For the normal co-valent structure of coumarin, assuming the usual values for the group moments of and C = O, the calculated value for the moment is 4·04 units ; see Fig. (3).

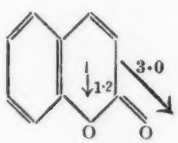
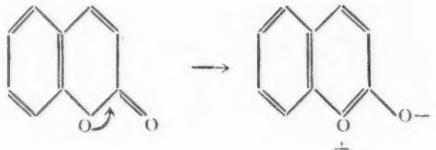


FIG. 3.

This value is only 0·5 units below the observed value of 4·5. On the theory

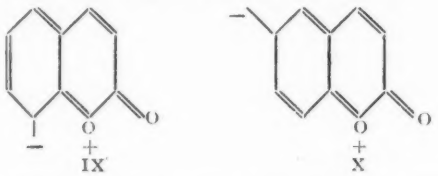
[15] E. C. E. Hunter and J. R. Partington, *Jour. Chem. Soc.*, 1934, 87.
[16] M. A. Govinda Rau, *Curr. Science*, 1936, 5, 132.

of electromerism, there will be in coumarin also a drift of electron from the $>O<$ to $C=O$, as indicated in Formula VII, leading to an excited state VIII.



VII VIII

The approximate moment for this excited state calculated with the usual interatomic distances will be 13×10^{-18}. This smaller value for the moment of the excited state may partly account for the low increment of the observed moment value over the calculated, but only partly. For though there are here only two unexcited canonical states possible, it is interesting to observe that some of the different excited structures will have their moments in the opposite sense to that in VIII, as in IX and X



IX X

The contribution of the most prominent excited state VIII will thereby be diminished and the net contribution of the excited states will be only a small factor.

As in the case of directed substitutions in the benzene ring, the excited phases of these molecules are mainly responsible for the types of substitutions in them, and the reactivities of the groups present. A more detailed study of the moments, and their exact orientations in these molecules is called for, before a complete analysis into the various component resonating structures could be made so as to lead to more quantitative conceptions regarding the reactivities of these molecules.

Summary.

(1) The moments of 2·6 dimethyl-γ-pyrone, xanthone, and coumarin have been determined in benzene solutions at 10°, 20°, 30° and 40° C. The values for 20° are 4·48, 2·93 and 4·51 respectively.

(2) The high moments for these pyrones are due to the state of resonance in which they exist, between the unexcited states of low moments and excited states of high moments.

(3) The difference in value between the moments of dimethyl-γ-pyrone and xanthone must be due to the greater number of unexcited parent states for the latter.

(4) The small difference between the calculated and observed moments for coumarin is due to the moments of some of the excited phases being in the opposite sense to the normal value.

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